STUDIES OF OXYGEN-HELIUM DISCHARGES FOR USE IN ELECTRIC OXYGEN-IODINE LASERS

BY

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DISSERTATION

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Abstract

In recent work, the performance of the **Electric Oxygen-Iodine Laser** (ElectricOIL), developed in partnership by researchers at the University of Illinois and CU Aerospace, has been greatly improved through systematic study of various components of this new laser technology. One major contribution to the advancement of ElectricOIL technology has been the development of electric discharges capable of producing significant flow rates of the precursor electronically-excited molecular oxygen, O$_2$(a$^1$Δ). O$_2$(a$^1$Δ) serves as an energy reservoir in the laser system, pumping atomic iodine by near-resonant energy transfer producing gain and laser on the I(2P$_{1/2}$) → I(2P$_{3/2}$) transition at 1315 nm. Initial experimental work with radio-frequency discharges showed the importance of controlling O-atom flow rates to reduce quenching losses of energy stored in O$_2$(a$^1$Δ), and determined proper selection of the helium diluent ratio and specific power deposition (power per O$_2$ flow rate). Further experimental investigations with transverse capacitive radio-frequency discharges in O$_2$/He/NO mixtures in the pressure range of 1-100 Torr and power range of 0.1-1.2 kW have indicated that O$_2$(a$^1$Δ) production is a strong function of geometry (transverse gap), excitation frequency, and pressure. These parameters along with gas flow mixture dictate the current density at which the discharge operates, and its modal characteristics (normal vs. abnormal, homogeneous vs. inhomogeneous). A key result is that to encourage efficient O$_2$(a$^1$Δ) production these parameters should be selected in order to promote a homogeneous (low current density) discharge. The discharge behavior is characterized using terminal current-voltage-characteristics, microwave interferometer measurements, and plasma emission intensity measurements. Numerous spectroscopic measurements of O$_2$(a$^1$Δ), oxygen atoms, and discharge excited states are made in order to describe the discharge performance dependent on various parameters. The influence of NO on O-atom flow rates and O$_2$(a$^1$Δ) production is investigated. Progress of laser power extraction since initial reports in 2005 is overviewed.
Acknowledgments

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# Nomenclature

Abbreviations:

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABL</td>
<td>Airborne Laser</td>
</tr>
<tr>
<td>AFRL</td>
<td>Air Force Research Laboratory</td>
</tr>
<tr>
<td>ATL</td>
<td>Advanced Tactical Laser</td>
</tr>
<tr>
<td>CAV</td>
<td>cavity</td>
</tr>
<tr>
<td>CCD</td>
<td>charge-coupled device</td>
</tr>
<tr>
<td>COIL</td>
<td>Chemical Oxygen-Iodine Laser</td>
</tr>
<tr>
<td>CW</td>
<td>continuous-wave</td>
</tr>
<tr>
<td>CUA</td>
<td>CU Aerospace (Champaign, IL)</td>
</tr>
<tr>
<td>CVC</td>
<td>current voltage characteristic</td>
</tr>
<tr>
<td>DC</td>
<td>direct current</td>
</tr>
<tr>
<td>DOIL</td>
<td>Discharge Oxygen-Iodine Laser</td>
</tr>
<tr>
<td>EEDF</td>
<td>electron energy distribution function</td>
</tr>
<tr>
<td>ElectricOIL</td>
<td>Electric Oxygen-Iodine Laser</td>
</tr>
<tr>
<td>EOIL</td>
<td>Electric Oxygen-Iodine Laser</td>
</tr>
<tr>
<td>HV</td>
<td>high voltage</td>
</tr>
<tr>
<td>ICRF</td>
<td>inductively-coupled radio frequency</td>
</tr>
<tr>
<td>ID</td>
<td>internal diameter</td>
</tr>
<tr>
<td>IG</td>
<td>internal gap</td>
</tr>
<tr>
<td>IP</td>
<td>ionization potential</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>IV</td>
<td>internal volume</td>
</tr>
<tr>
<td>LBHP</td>
<td>liquid basic hydrogen-peroxide</td>
</tr>
<tr>
<td>LCCRF</td>
<td>longitudinal capacitively-coupled radio frequency</td>
</tr>
<tr>
<td>LIF</td>
<td>laser-induced fluorescence</td>
</tr>
<tr>
<td>MN</td>
<td>matching network</td>
</tr>
<tr>
<td>MW</td>
<td>mega-watt</td>
</tr>
<tr>
<td>MWI</td>
<td>microwave interferometer</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared</td>
</tr>
<tr>
<td>OMA</td>
<td>optical multi-channel analyzer</td>
</tr>
<tr>
<td>OT</td>
<td>optical transparency</td>
</tr>
<tr>
<td>PC</td>
<td>positive column</td>
</tr>
<tr>
<td>PMT</td>
<td>photomultiplier tube</td>
</tr>
<tr>
<td>PP</td>
<td>partial pressure; PP(X) := partial pressure of X</td>
</tr>
<tr>
<td>PSI</td>
<td>Physical Sciences, Inc. (Andover, MA)</td>
</tr>
<tr>
<td>RF</td>
<td>radio frequency</td>
</tr>
<tr>
<td>SOG</td>
<td>singlet-oxygen generator</td>
</tr>
<tr>
<td>TAA</td>
<td>trace argon actinometry</td>
</tr>
<tr>
<td>TALIF</td>
<td>two-photon absorption laser-induced fluorescence</td>
</tr>
<tr>
<td>TCCRF</td>
<td>transverse capacitively-coupled radio frequency</td>
</tr>
<tr>
<td>Td</td>
<td>Townsend units, 1 Td = 1x10^{-17} V-cm²</td>
</tr>
<tr>
<td>TDLS</td>
<td>tunable diode laser spectroscopy</td>
</tr>
<tr>
<td>TRGES</td>
<td>trace rare gas emission spectroscopy</td>
</tr>
</tbody>
</table>
Variables:

\(A\)  area, typically of electrode
\(A_{ij}\)  spontaneous emission rate from state i to state j
\(B_X\)  susceptance of X
\(B\)  magnetic field (flux density)
\(C_X\)  capacitance of X, or a constant
\(d\)  transverse discharge gap
\(d_q\)  quartz wall thickness
\(d_s\)  sheath thickness
\(d_l\)  positive column thickness, \(d - d_s\)
\(e\)  electron charge
\(E/N\)  electric field to gas density ratio
\(E\)  electric field
\(f\)  excitation frequency or electron energy distribution function
\(F(\varepsilon)\)  normalized electron energy distribution function
\(F_{\text{cal}}\)  calibration factor relating intensity to density
\(F\)  Lorentz force
\(g_i\)  degeneracy of state i
\(g_{th}\)  gain coefficient threshold for laser power extraction
\(g_0\)  small signal gain coefficient
\(G_X\)  conductance of X
\(H\)  magnetic field (field intensity)
\(I\)  current, or intensity
\(J\)  rotational quantum number, or current density magnitude
\(J\)  current density
\(k_X\)  kinetic rate for process X
\(K_{eq}\)  temperature dependent equilibrium constant of \(O_2(a) \rightarrow I^*\)
\(L_g\)  gain length
\(L_X\)  inductance of X, or a path length
\(m\)  exponent in power approximation for gas heating, \(T \sim J^m\)
\(m_e\)  electron mass
\(M\)  variable gas (in reaction), or mass of gas species
\(n_e\)  electron density
\(n_i\)  ion density
\(n_X\)  molar flow rate of species X
\(N\)  gas density, or normalized electron density
\(N_{\text{gas}}\)  gas density
\(p\)  pressure
\(P_{\text{out}}\)  output laser power
\(P_{O_2(a)}\)  power carried by \(O_2(a)\) flow
\(P_X\)  power associated with X
Q  gas quencher
ri  reflectivity of mirror i
R  reflection coefficient
RX  resistance of X
RFsys  RF system power, power into matching network
S  normalized collision frequency
t  time
ti  transmissivity of mirror i
T  gas temperature or transmission coefficient
Te  electron temperature
Tg  gas temperature
u  flow velocity
UCl  chlorine utilization fraction
v  vibrational quantum number
v(ε)  electron velocity as a function of energy
v  electron thermal velocity
V  voltage
we  mean electron energy
W  specific energy deposition, J per mmol of O2
ΔW  energy loss of elastic collision
Y  fractional yield of O2(a)
YOT  optical transparency O2(a) yield
YX  admittance of X
ZX  impedance of X

α  first Townsend ionization coefficient, denotes homogeneous transverse discharge; or attenuation per unit length
β  phase shift per unit length
γ  secondary electron emission coefficient, denotes inhomogeneous transverse discharge; or complex propagation coefficient; or gain coefficient
δ  diffraction loss term (due to aperture)
ε  electron energy
εk  electron characteristic energy
εG  gas characteristic energy
εth  electron energy threshold for electron-impact process
ε0  permittivity of free space
εq  relative permittivity of quartz
ϕ  phase shift
σc  plasma conductivity
σij  energy dependent cross section for excitation of state j from state i
σ(T)  temperature-dependent stimulated emission cross section
ηX  efficiency of process X
vm  collision frequency
v_inel  inelastic collision frequency
\[ \omega \] RF excitation frequency
\[ \omega_p \] plasma electron frequency
\[ \mu_0 \] permeability of free space
\[ \mu_q \] relative permeability of quartz

Additional Subscripts and Superscripts:

abs absorbed
AG air glow (due to O-NO recombination)
avg averaged value
b backward
BX bridge circuit hybrid channel X
cav cavity
cor corrected
chem chemical
cr critical
det detector
dis discharge
diss dissociation
e electron
eff effective
elec electrical
f forward
g gas, or gain
i ion
inel inelastic
inv inversion
I imaginary part
max maximum
min minimum
\[ n_\alpha \] normal \( \alpha \)-mode
obs observed
p plasma
plate measured across electrode plates, or into electrode plate
q quartz
Q quencher Q
r relative
R real part, or reference (depending on context)
refl reflected
RMS root mean squared
s sheath or source
sat saturation
se superelastic
stray stray current or capacitance
sys system
<table>
<thead>
<tr>
<th>term</th>
<th>measurement at/across terminals (electrodes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>th</td>
<td>threshold</td>
</tr>
<tr>
<td>titr</td>
<td>titration</td>
</tr>
<tr>
<td>trans</td>
<td>transport</td>
</tr>
<tr>
<td>T</td>
<td>total (referring to current)</td>
</tr>
<tr>
<td>V</td>
<td>vessel</td>
</tr>
<tr>
<td>0</td>
<td>no plasma or free-space</td>
</tr>
<tr>
<td>-</td>
<td>left-running (negative)</td>
</tr>
<tr>
<td>+</td>
<td>right-running (positive)</td>
</tr>
<tr>
<td>*</td>
<td>excited state</td>
</tr>
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</table>
1. Introduction and Background

This work describes the development of electric discharges in oxygen-helium mixtures for use in Electric Oxygen-Iodine Lasers (ElectricOIL). The ElectricOIL is an all-gas phase electronic energy transfer laser in which singlet-delta oxygen, a molecular electronic state at 0.977 eV denoted O₂(a¹Δ), is excited by electron impact of ground-state oxygen, and then mixed with iodine vapor which is dissociated and pumped by near-resonant energy transfer to the I(⁵P₁/₂) electronic state (0.943 eV). If the O₂(a¹Δ) yield is high enough for laser cavity temperature conditions, a population inversion of the I(⁵P₁/₂) state compared to the atomic iodine ground state is sustained, gain is achieved in the cavity, and laser power can be extracted at 1315 nm. The principal kinetics of the device are:

1) Electron impact of ground state O₂ to create singlet-delta oxygen:

\[
e^- + O₂(X^3Σ) \rightarrow O₂(a¹Δ) + e^- \quad (R. 1.1)
\]

2) Dissociation of molecular iodine vapor by excited O₂ or O-atoms (or electrons in secondary discharge):

\[
I₂ + O₂* \rightarrow 2 I + O₂ \quad (R. 1.2.a)
\]
\[
I₂ + O \rightarrow IO + I
\]
\[
IO + O \rightarrow O₂ + I \quad (R. 1.2.b)
\]
\[
e^- + I₂ \rightarrow 2 I + e^- \quad (R. 1.2.c)
\]

3) Pumping of atomic iodine by excited oxygen:

\[
O₂(a¹Δ) + I(⁵P₃/₂) \Leftrightarrow O₂(X^3Σ) + I(⁵P₁/₂) \quad (R. 1.3)
\]

4) Stimulated emission of electronically excited iodine to extract laser power at 1315 nm:

\[
hν + I(⁵P₃/₂) \rightarrow I(⁵P₅/₂) + 2 hν \quad (R. 1.4)
\]

ElectricOIL is derived from the classic Chemical Oxygen-Iodine Laser (COIL) in which O₂(a¹Δ) is created by chemical means [1.1]. Here in this section, background on the development and application of oxygen-iodine lasers will be given. Then the basic system configuration of the ElectricOIL device will be described. After this, the ongoing research and development of ElectricOIL by the group at the University of Illinois at Urbana-Champaign (UIUC) and CU Aerospace (Champaign, IL) will be discussed. Finally, the experimental studies reported on in this thesis will be introduced.
1.1. Oxygen-Iodine Laser Background

The first oxygen-iodine laser was introduced in work by McDermott [1.1] at Air Force Weapons Laboratory (now Air Force Research Laboratory, AFRL). This system produced $\text{O}_2(a^1\Delta)$ (denoted hereafter as $\text{O}_2(a)$) by means of a chemical process at an interface between gaseous chlorine and liquid basic hydrogen peroxide (BHP), and achieved an output power of $\sim 4 \text{ mW}$. A comprehensive history of the development of COIL technology in the United States between 1960 and the mid 1990s was provided by Truesdell [1.2].

Since the introduction of this type of system called COIL (for Chemical Oxygen-Iodine Laser) the technology has been scaled to the order of a mega-watt (MW), and is the current primary laser system of choice for the Airborne Laser program (ABL) which integrates a high-power COIL into a Boeing 747-400 [1.3]. The mission of the ABL is to detect, track, target, and destroy ballistic missiles shortly after launch (during the boost phase); the ABL’s beam control/fire control system focuses the MW-class COIL beam on a pressurized area of the boosting missile long enough for the concentrated beam energy to cause a structural failure [1.3]. The COIL is also used as the primary laser in the Advanced Tactical Laser (ATL) program, where a 10 kW-class COIL is integrated into a C-130H cargo aircraft [1.4]. The operational goal of the ATL is a precision, speed-of-light destructive capability which greatly reduces collateral damage compared to conventional weapons [1.4]. In contrast to the ABL which is designed for long-range, high-power missions and vents its laser-system exhaust to the atmosphere, the ATL traps and reprocesses the exhaust [1.4]; this allows the laser platform to operate at any altitude and use the reprocessed exhaust in more firings [1.4]. The COIL is also of interest for use in commercial applications because it is a continuous-wave (CW) scalable laser with a fiber-deliverable wavelength (1.315 $\mu$m) [1.5]; some commercial industrial applications are shipbuilding, automotive manufacturing, underwater cutting, and cutting tasks associated with decommissioning and decontaminating nuclear facilities [1.5].

Chemical lasers like COIL are an excellent choice for strategic and tactical operations, considering the capabilities of high output power and operation at near-infrared wavelength which allows for better beam propagation in turbulent atmospheric conditions and is less damaging to the human eye [1.6]. COIL offers a few advantages because it is an electronic metastable energy transfer laser rather than a purely chemical laser like HF/DF,
where the laser energy is stored in the vibrational stretching of the H-F bond [1.7]. The electronic transition in COIL is 0.943 eV compared to the vibrational energy transitions which release radiation in HF lasers, 0.458 eV (for \(v'' = 1, v' = 0\)) and 0.438 eV (for \(v'' = 2, v' = 1\)). The resulting laser transition occurs at a lower wavelength, 1.315 µm compared to 2.71 µm (0.458 eV) and 2.83 µm (0.438 eV); this shorter wavelength device offers higher power per mass of reagents, reduced beam divergence due to diffraction, and better atmospheric transmission [1.7]. Compared to HF lasers, the COIL is a lower gain device (~1%/cm compared to ~20%/cm). The high gain of HF can be attributed to the distribution of vibrational states resulting from the reaction \(F + H_2 \rightarrow HF(v) + H\), 12:20:6:1 for \(v = 3:2:1:0\) [1.7], favoring population of \(v = 1\) to 3 over \(v = 0\) by 38 to 1 (a similar distribution occurs in DF lasers which operate at 3.8 µm due to lower vibrational energy). The low gain of the COIL can be attributed to the near-resonant behavior of the pumping reaction of I* by \(O_2(a)\) which continuously sustains the iodine population inversion at a relatively low value (dependent on temperature and \(O_2(a)\) level). COILs therefore operate nearer to threshold where optical losses have larger influence on efficiency, but are allowed longer gain media and greater geometrical scaling for high power performance [1.7].

Thus, the COIL has desirable wavelength and efficiency characteristics, and exhibits good beam quality and scalability, making it a good choice for airborne strategic and tactical operations [1.3, 1.4]. However, there are a number of logistic concerns related to the heavy aqueous fuels required and the heat exhaust generated when the weapon is fired [1.6]. Thus, numerous investigations have been made towards the handling of such issues as airborne laser system power/fuel consumption and exhaust management (see for example Adams and Nairus [1.8]). Although chemical lasers such as COIL have thermal management advantages over other high-energy lasers such as solid-state or high-power microwave devices, the logistics of chemicals as the stored energy reservoir create a major disadvantage [1.8]. The solution to these logistical issues is a laser system which maintains the thermal properties of high-energy chemical lasers, but eliminates the use of bulky, hazardous chemical fuels.

One such approach is a system which replaces the heavy chemical \(O_2(a)\) generation system of COILs with an electric gas discharge generation scheme for \(O_2(a)\) generation. Carroll et al. [1.9.a-c] made the first successful gain and laser demonstration in a system of this type, referring to it as ElectricOIL (for Electric Oxygen-Iodine Laser). In this system,
$O_2(a)$ was produced in a flowing radio-frequency (RF) discharge in a gaseous mixture of oxygen, helium, and nitric oxide. The influence of trace amounts of NO in the discharge is to suppress the level of oxygen atoms which quench $O_2(a)$ and $I^*$. Downstream of the discharge, molecular iodine was injected and then dissociated by excited states in the discharge effluent, and pumped to the lasing state by the $O_2(a)$ produced within the discharge. As in classic COIL, a supersonic expansion laser cavity was used to lower the temperature, which shifts the equilibrium between $O_2(a)$ and $I(^3P_{1/2})$ in favor of $I(^3P_{1/2})$ (denoted $I^*$ hereafter). Other devices of this type are typically referred to as EOIL or DOIL (for Electric or Discharge Oxygen-Iodine Laser). Hicks et al. [1.10] have demonstrated a DOIL similar to ElectricOIL using a pulsed discharge technique, while Rawlins and Davis [1.11] have measured positive gain in both subsonic and supersonic flow systems using microwave discharges. Other groups are developing DOIL technology, including work at AFRL led by Hill [1.12], and work by groups in Russia at Moscow State University (Braginsky [1.13]) and Lebedev Physical Institute (Ionin [1.14]). Ionin recently published an in-depth topical review of singlet oxygen production in low-temperature plasma, which documents the efforts of numerous groups studying oxygen discharges applicable to DOIL technology [1.14].

Of the works cited by Ionin, it is important to mention the efforts of Zalesskii [1.15] and Fournier [1.16]. Zalesskii originally conceived the idea of DOIL, and introduced much of the relevant kinetic theory; Zalesskii envisioned and tested a compact pulsed DC system, consisting of an oxygen and iodine vapor discharge excited in a small tube with high-reflectivity mirrors at either end [1.15]. Fournier et al. proposed and tested an electron-beam driven system, shown in Fig. 1.1 that resembled the first operational systems [1.9, 1.10]. Neither of these attempts was successful, but these laid some of the early groundwork for the current DOIL systems under development [1.14].
In the works of Zalesskii [1.15] (1973) and Fournier et al. [1.16] (1980), detailed analytical and computational analyses of the proposed laser systems were made, but the conditions required for positive gain (and therefore laser power extraction) were not achieved. Zalesskii tested a (no flow) pulsed system consisting of a 16 mm diameter 50 cm long discharge tube operating from a 1-\(\mu\)F capacitor charged to 30 kV, with the discharge passing through a mixture of 10 Torr oxygen and 0.3 Torr of iodine. The system had a max current of 250 A and a current-pulse duration of 150 \(\mu\)s [1.15]. The absorption through the discharge tube at 1315 nm was measured as a function of time during the discharge pulsing using a CF\(_3\)I photodissociation laser with 1.2 \(\mu\)s pulse duration [1.15]. Three regimes were observed during the discharge pulse and afterglow periods (time between pulses): (1) during the first 100 \(\mu\)s --- 20-30% absorption dependent on the detector aperture, (2) during the next 100-150 \(\mu\)s --- induced optical transparency, and (3) during the following 600-800 \(\mu\)s -- gradual attenuation of the beam to a practically stationary level corresponding to the calculated absorption with full dissociation of initial iodine input [1.15]. A control experiment with the oxygen replaced with argon was also performed in which the second phase (transparency) was not achieved, indicating that significant pumping of I* occurred due to oxygen in the period at the end of the discharge pulse and beginning of the afterglow [1.15]. The three observed regimes are consistent with (1) initial dissociation of the iodine by electron impact during the discharge pulse, (2) pumping of I* approaching \([I^*] = 0.5 [I]\) (optical transparency) as O\(_2\)(a) builds up at the end of the pulse and remains during the afterglow, and (3) O\(_2\)(a) decays removing I* pumping, but iodine dissociation is maintained by other excited species in the afterglow. Although I* pumping was demonstrated in this
pulsed no-flow system, gain was not achieved, and laser power extraction attempts with a high-Q resonator were unsuccessful [1.15].

Fournier et al. analyzed and tested a flowing electron beam sustained system, modeling the system electron impact kinetics in O₂/Noble gas mixtures using a Boltzmann code [1.16]. In modeling of the system, population inversion was not achieved, but I* was sustained in mixing of I₂ downstream of the discharge effluent containing O₂(a) [1.16]. The experimental work with the electron beam in O₂/Ar and O₂/Ne mixtures resulted in current instabilities [1.16]. However, it was predicted that population inversion might be possible in this system if a supersonic expansion was introduced in order to control pumping of iodine [1.16].

From this early work with electrically-pumped oxygen iodine laser concepts, it seemed that construction of an operational system was feasible [1.15, 1.16]. However, despite the detailed modeling of each system, experimental attempts to achieve gain and laser extraction failed. In the case of Zalesskii’s system [1.15], the problems were likely due to lacking of necessary diagnostic techniques, considering that the only diagnostic reported was absorption of the discharge medium at 1315 nm. The data taken indicated that I* was being pumped in the afterglow (optical transparency), but also that the iodine dissociation was maintained after I* decayed (absorption level indicating full dissociation in ground state). Thus in the afterglow of the discharge, some mechanism was removing energy that should have been stored in O₂(a). Use of diagnostic techniques for excited species (O₂(a), O₂(b), oxygen atoms, I*, etc.) might have allowed a more detailed understanding to determine the source of the quenching. In the case of Fournier et al. [1.16], the modeling indicated a viable system (if supersonic expansion could be used), but experimental attempts were not effective because of the discharge instabilities, and therefore no information about O₂(a) production or I* pumping was obtained. Some lessons to be learned from these early attempts are:

1. Modeling of the system is not adequate unless a broad understanding of the kinetics is obtained through experiment.

2. The kinetics of an electric oxygen-iodine laser system are complex, and understanding of system kinetics is enhanced by diagnostic techniques for known species.

3. A well-performing (stable) discharge is required to obtain useful results and determine how an electric oxygen-iodine laser can be realized.
1.2. The Basic Components of an ElectricOIL Device

A schematic of the basic configuration of the first operational ElectricOIL is shown in Figure 1.2. The similarities to the system proposed by Fournier et al. [1.16] are readily seen. A mixture containing oxygen is flowed into a RF discharge chamber. Within the discharge chamber, the pre-cursor \( \text{O}_2(a) \) is produced by electron impact. The \( \text{O}_2(a) \)-rich flow which exits the discharge chamber is chilled in a heat-exchanger region, then enters a mixing region where molecular iodine is injected. The mixing of the \( \text{O}_2(a), \text{O}_2(b) (\text{O}_2(b^1\Sigma), \text{electronic state at 1.63 eV}) \) and oxygen atoms from the discharge with iodine results in iodine being dissociated and pumped by near-resonant energy transfer with \( \text{O}_2(a) \) to the desired \( \text{I}^* \) state. The flow is then mixed with chilled \( \text{N}_2 \) diluent and expanded to supersonic through a nozzle. The expanded flow passes into a cavity containing high-reflectivity mirrors, and if conditions are correct for positive gain, laser power can be extracted at 1315 nm.

![Figure 1.2. Schematic of the ElectricOIL system developed by CU Aerospace and the University of Illinois (Carroll et al. [1.9]).](image)

In the work of Carroll et al. [1.9], two key mechanisms were introduced that allowed positive gain to be achieved: (i) a Mach 2 supersonic nozzle was used to expand the flow, lowering the temperature significantly to shift the equilibrium of the pumping reaction in favor of \( \text{I}^* \), lowering the \( \text{O}_2(a) \) yield threshold required for positive gain, and (ii) a small quantity of NO was introduced to the discharge flow which depleted the level of oxygen atoms in the system reducing quenching mechanisms of both \( \text{O}_2(a) \) and \( \text{I}^* \), and greatly reduced production of ozone which is a rapid quencher of \( \text{O}_2(a) \). Thus, by introduction of these simple mechanisms, the power flow into \( \text{I}^* \) was improved enough to achieve a population inversion (\([\text{I}^*] > 0.5[\text{I}]\)) in the laser cavity. The understanding of the rapid \( \text{I}^* \)
quenching by atoms was obtained by detailed experimental analysis of the mixing of iodine with the species in the afterglow of the RF discharge [1.9]. The basic components of an operational ElectricOIL device are as follows:

1. A well-sustained discharge in which sufficient O$_2$(a) yield is produced to create positive gain at the laser cavity temperature
2. A gas flow mixture which allows efficient O$_2$(a) production, and reduces oxygen atoms which quench power from the system
3. A heat-exchanger/coolant injection system which lowers flow temperature
4. A supersonic expansion which further lowers the temperature and increases the gain above threshold for laser power extraction

1.3. Ongoing ElectricOIL Research Efforts

Since the first ElectricOIL configuration was developed [1.9], research on devices of this type have continued. The first ElectricOIL had an output power of 220 mW at a gain level of 0.0067 %/cm. In a period of less than five years, the laser performance was improved to an output of 28 W and a gain level of 0.22 %/cm (maintaining 5 cm gain length) [1.17]. The engineering investigations that have led to these improvements involved: (i) diagnostic development, (ii) discharge behavior studies and optimization, (iii) studies of system kinetics, (iv) discharge scaling, (v) heat-exchanger development, and (vi) laser power extraction analysis. In this thesis the first three of these areas, diagnostic development, discharge optimization, and system kinetics studies will be given priority, and the other areas will be covered briefly. These remaining topics will be addressed in proceeding work by others as work on ElectricOIL continues.

Studies of the oxygen-helium discharges used in ElectricOIL, and development of diagnostics for the device were a key element in understanding the system dynamics, and making the first gain and lasing of an ElectricOIL possible. Basic understanding of most components downstream of the singlet-oxygen generator (SOG) could be taken from work with COIL. However, experimental and computational studies of the discharge were necessary in order to address two important questions:

1) How could O$_2$(a) production in a gas discharge be optimized?
2) What is the influence of other species formed on system kinetics?
Thus it was important to have diagnostics for O$_2$(a) measurement, but also to have systems in place for the study of mechanisms resulting from the discharge “by-products”.

Preceding the first successful ElectricOIL device developed by the group at UIUC and CU Aerospace (UIUC/CUA) [1.9.a-c], a number of researchers had shown that significant levels of O$_2$(a) could be produced in flowing gaseous discharges [1.14]. Benard and Pchelkin reported 11% yield using a microwave discharge [1.18]. Fujii reported a yield of 17% with a radio-frequency (RF) discharge [1.19]. Researchers from Fujisaki Electric (Itami et al. [1.20]) showed evidence of 21% O$_2$(^1Δ) yield using a microwave discharge. Hill reported 16% yield with a controlled-avalanche discharge [1.21]. Schmiedberger reported 32% yield at low-pressure (0.43 Torr) using an RF discharge [1.22]. In early work, the UIUC/CUA group (Verdeyen [1.23]) reported a O$_2$(^1Δ) yield of ~16% in flowing RF discharge experiments at a pressure of 2 Torr. Thus, at the time it was quite possible to attain the O$_2$(a) yields necessary for producing a population inversion in iodine.

However, as will be discussed further in the next section, the excitation of O$_2$(a) in an electric discharge is a complicated process. The key to optimization is to construct a discharge that has an $E/N$ (electric field-to-gas density ratio) that favors the production of the desired O$_2$(a) state which has an electron-impact threshold at 0.977 eV above the ground state. The discharge $E/N$ is characteristic of the electron energy distribution function (EEDF) which describes the state of the electron gas within the plasma. Regardless of how well this distribution is controlled to optimize for O$_2$(a) production, the distributed energy of the electron gas results in a variety of processes taking place within the discharge, and the state of the gas flow exiting the discharge region is not simply a flow consisting primarily of O$_2$(a) and O$_2$(X) (as in COIL singlet-oxygen generation). Instead, the condition of the flow exiting the discharge is subject to the energy deposited by the electron gas into a variety of states. These include:

- Vibrational and rotational energy
- Thermal energy (gas temperature)
- Energy stored in electronic energy states of molecules and atoms
- Dissociated molecules

This is a complicated situation, and must be dealt with accordingly. Unfortunately it is not possible to treat the discharge as a “black-box” which produces significant O$_2$(a) for
sustaining a population inversion in atomic iodine. It is also necessary to understand how energy is transferred into the other processes in the discharge, and how the “byproducts” of these processes influence the system kinetics, primarily the maintenance of O$_2$(a) levels in the system, the transfer of the energy stored in O$_2$(a) into the I$^*$ laser state, and the influence of atomic oxygen.

In early work by the group at UIUC and CU Aerospace (UIUC/CUA) [1.9.b], it was realized that a primary culprit which depleted the energy stored in O$_2$(a) was the significant level of oxygen atoms (O-atoms) exiting the discharge. The critical behavior is that the laser state I$^*$ is rapidly quenched by O-atoms; therefore, once iodine was added to the O$_2$(a) rich flow, energy was transferred to I$^*$ which was in turn rapidly deactivated by O-atoms, and the resonant energy transfer between O$_2$(a) and I$^*$ (Reaction 1.3) was not maintained, due to loss of the power carried by O$_2$(a). This issue will be covered more thoroughly in Section 5.

The negative influence of I$^*$ + O $\rightarrow$ I + O quenching reaction on the system dynamics made it necessary to investigate diagnostic techniques for measuring oxygen atoms. Thus, a few different diagnostic techniques were taken from other experimental investigations in the literature and applied to work with discharges used in ElectricOIL development by the UIUC/CUA group. These included O-NO airglow techniques and argon actinometry techniques [1.24]. Both of these techniques were applied along with a variety of other diagnostics throughout the various phases of ElectricOIL development from the initial configurations that first resulted in gain and laser [1.9], to the more recent configurations operating at 10s of watts [1.17]. The result of these investigations was to introduce NO$_X$ (NO or NO$_2$) to the system which leads to enhancement of O$_2$(a) production and reduces the flow rate of oxygen atoms by recombination reactions [1.9.b, 1.24].

After gain and laser action were achieved, it became necessary to further develop the discharge technique being applied for O$_2$(a) production. The initial concept made use of a large-gap (25.4 cm) longitudinal radio-frequency (RF) discharge [1.9]. This device worked at low discharge pressures, but to improve power output it is necessary to raise the oxygen flow rate of the device which results in higher pressure operation. At higher pressure, the large-gap longitudinal concept did not work well, and was prone to thermal arcing. A variety of other discharge configurations were investigated including microwave-induced, inductive RF, transverse-capacitive RF, and pulser-sustainer concepts. All of these concepts were
shown to be capable of producing O_2(a) sufficient for creating an ElectricOIL [1.9, 1.10, 1.11, 1.25]; however, the transverse-capacitive RF discharge proved to be the most robust system and the easiest to adapt for high pressure operation [1.26, 1.27].

With the transverse RF discharge chosen as the most suitable discharge configuration for ElectricOIL development by UIUC/CUA, a detailed configuration study of the influence of various discharge parameters on O_2(a) production was conducted. The parameters that proved important in optimizing O_2(a) production were (i) operating pressure, (ii) transverse gap, (iii) discharge flow length (or residence time), and (iv) excitation frequency. The key result of the work was that in order to achieve efficient production of O_2(a), a uniform (homogeneous), normal-mode glow discharge must be maintained [1.26]. In the normal-mode glow discharge, low current density is maintained, and as more power is applied to the discharge, the volume of plasma in the tube between the plates increases proportionally, maintaining a similar current density for increased power deposited while voltage remains about constant. If the plasma fills the volume between the plates and is confined, the discharge is then forced into an abnormal mode in which the plasma voltage and current density rise in unison. This simple transition from a normal to an abnormal mode can severely decrease the O_2(a) production efficiency. However, the onset of this transition can be delayed by careful selection of the transverse discharge parameters (i) – (iv). Additionally, there is a constriction of the normal-mode discharge to high current density at high pressure which must be avoided by proper selection of the frequency and gap. A variety of diagnostics were used to study the dynamics of this transition including various excited state measurements, airglow (O-NO recombination) and actinometry measurements, plasma glow distribution measurements, and plasma density and collision frequency measurements using a microwave interferometer.

Optimization of O_2(a) production, and study of various additional excited species and oxygen atoms in transverse-capacitive RF discharges has allowed operation of ElectricOIL devices to higher operating flow rates and pressures of oxygen and allowed substantial improvement in the laser power output [1.17]. The primary goals of this thesis are as follows:

(1) Summarize the ElectricOIL system kinetics.
(2) Explain the diagnostic techniques applied in experiments, especially those for oxygen atoms.

(3) Review and discuss early ElectricOIL work to highlight lessons learned.

(4) Report on behaviors of transverse discharges in O₂:He:NO mixture and describe how to optimize for O₂(a) production.

(5) Report on the influence of NO on O₂(a) production and oxygen atom suppression.

(6) Report and discuss laser power extraction experiments.

1.4. Research Plan

The research plan which led to the key findings of this thesis work was:

- **Investigate the parameters which drive production of O₂(a) in moderate pressure transverse RF discharges in O₂/He/NO mixture.** In particular, determine the influence of pressure, gap and frequency on discharge modes (normal-abnormal, homogeneous-inhomogeneous) and relate these behaviors to O₂(a) and O-atom production.

- **Measure electrical parameters (E/N, nₑ) of RF discharge in typical ElectricOIL O₂/He mixture.** Compare terminal electrical measurements and microwave interferometer measurements.

- **Study the influence of nitric oxide on O₂(a) and O-atoms.** Measure the removal of dominant quenching species (O, O₃). Investigate experimentally the “boost” in O₂(a) production observed when trace NO is introduced to the discharge flow.

- **Conduct gain and laser power experiments which expose power extraction issues associated with ElectricOIL technology.** Measure the gain “recovery” downstream of a resonator for comparison to modeling results using standard oxygen-iodine laser kinetics.

1.5. Thesis Overview

The remainder of this thesis is laid out in a number of sections discussing the theory of ElectricOIL, the design of RF discharges used to excite O₂(a), the diagnostic techniques used to analyze the system, and summaries of various experimental studies performed. These sections are summarized briefly here.
In Section 2, the ElectricOIL kinetics and theory will be discussed, beginning with the resonant energy transfer from O$_2$(a) to I$^*$. Then the theory of the production of excited states in the discharge will be overviewed, and the system kinetics will be discussed, focusing mainly on the production of O$_2$(a), O$_2$(b) and oxygen atoms, and on the influence of NOX species when used in the discharge. The theoretical limits of O$_2$(a) production due to superelastic collisions will be explained, and the influence of oxygen atoms on quenching of power in the system will be described.

In Section 3, the circuit design and analysis of various discharges used in ElectricOIL will be overviewed. The goal of this section is to introduce various RF configurations (inductive, hollow-cathode, capacitive, transverse capacitive). The power supplies and circuit probe hardware used will be overviewed and the various circuits used to match the RF supply to the discharge vessel will be described and analyzed.

In Section 4, the optical diagnostics and diagnostic techniques used to investigate ElectricOIL will be overviewed. Some diagnostics, such as the “off-the-shelf” spectrometers and absorption diagnostics will be discussed briefly, giving basic theory and references to manufacturers and other important sources. Where more detail is required, as in the absolute intensity calibration of O$_2$(a) density from 1268 nm emission, the calibration technique and experimental procedure will be fully described. Other techniques, such as the O-NO airglow measurements or the argon actinometry techniques will also be discussed in more detail, giving background literature, information about components, descriptions of the theories applied, and overview of the calibration technique. The overall purpose of this section is to serve as a detailed introduction and summary of the variety of diagnostics used.

In Section 5 the early work on ElectricOIL discharge development will be covered. The purpose of this section is to overview the experimental studies that led up to the first ElectricOIL, to highlight the fundamental aspects that make the system possible, and how understanding of those aspects was developed. This discussion will focus somewhat on development of the understanding of the system kinetics, and aspects of ElectricOIL discharge configurations which produced positive results.

Sections 6-9 will address more specific experimental studies that were performed on the ElectricOIL system. The first of these, Section 6 will overview experimental studies of the transverse RF discharge, and describe fully how design parameters of the transverse
discharge influence $O_2(a)$ production. In Section 7, the influence of NO on the system will be described. In particular the effects discussed will be: (i) enhancement of $O_2(a)$ production, (ii) removal of oxygen atoms, and (iii) the influence on electrical parameters and excited state behavior. Section 8 will discuss experimental investigations in which microwave interferometer was used to measure the plasma density and collision frequency in an ElectricOIL transverse RF discharge configuration. Section 9 will summarize recent improvements in the gain and laser performance (beginning with initial demonstrations). Finally, Section 10 will conclude, providing perspective drawn from the results discussed here, highlighting key findings of the research, and offering suggestions for future investigations.

References


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[1.15] Zalesskii Yu 1975 A discharge laser operating on the iodine 1315-nm transition Sov. Phys. JETP 40 1


2. ElectricOIL Kinetics and O2(a) Production Theory

This section will discuss the kinetics of ElectricOIL. To begin with, the temperature-dependent pumping of the laser state I* by O2(a) will be overviewed. Then the production of O2(a) and other states within an electric discharge will be explained, discussing the energy levels of molecular oxygen, the cross-sections for important processes, and the dependence of electron-impact kinetics on the electric field-to-gas density ratio (E/N). Then, the typical saturation behavior of O2(a) with power input to a discharge will be explained. Finally, the important kinetics of the afterglow will be discussed, focusing mainly on the influence of oxygen atoms which quench the energy stored in O2(a).

2.1. The Oxygen-Iodine Laser Pumping Reaction

The key relationship in developing oxygen-iodine laser technology is the equation for the equilibrium rate determined from the forward and backward rates of the pumping reaction between O2(a) and I*. This equation relates the threshold O2(a) yield required as a function of temperature to achieve “optical transparency” on the iodine transition at 1315 nm, which requires [I*] = 0.5[I] (determined by the degeneracies of the upper and lower electronic states). The kinetics and associated temperature-dependent rates (see Palla et al. [2.1]) are as follows:

\[ O_2(a) + I \rightarrow I^* + O_2, \quad k_1 = k_{\text{forward}} = 2.3 \times 10^{-8}(T^{-1}) \text{ cm}^3/\text{s} \quad (R. 2.1) \]

\[ O_2 + I^* \rightarrow I + O_2(a), \quad k_2 = k_{\text{backward}} = 3.1 \times 10^{-8}(T^{-1}) \exp(-403/T) \text{ cm}^3/\text{s} \quad (R. 2.2) \]

Ignoring secondary processes, the time rate of change in [I*] due to Reactions 2.1 and 2.2 is given by

\[ \frac{d[I^*]}{dt} = k_1[I_2(a)][I] - k_2[I_2][I^*] \quad (\text{Eqn. 2.1}) \]

At steady-state equilibrium, this results in the expressions for the equilibrium rates and optical transparency O2(a) yield being respectively

\[ K_{eq} = \frac{k_1}{k_2} = \frac{[I^*][O_2(X)]}{[I][O_2(a)]}, \quad \text{and} \quad Y_{OT} = \frac{[O_2(a)]}{[O_2(a)]+[O_2(X)]} = (1+2K_{eq})^{-1} \quad (\text{Eqn. 2.2}) \]

This expression for \( Y_{OT} \) is plotted in Figure 2.1. The production of gain in an oxygen-iodine laser system requires significant O2(a) yields and low flow temperatures. At room
temperature (~300 K), an O₂(a) yield of approximately 15% is required to achieve positive gain ([I*] > 0.5 [I]). Thus early COILs [2.2, 2.3], which were room temperature devices required O₂(a) yields of ~15% or greater, and were scaled in power by increasing the gain length (referred to as exact “sewer pipe quantum engineering” by Truesdell [2.4]). However, the kinetics of the pumping reaction establish that the O₂(a) yield required for optical transparency decreases significantly with temperature. Thus, early in the development of COILs, supersonic nozzles were used to expand the flow to lower temperature (the first was ReCOIL in 1984, see Truesdell [2.4]); this allowed reduction in the size of the device (gain length), improvement in chemical efficiency due to lower cavity temperature, and stream-wise stretching of the gain medium which reduced density gradients in the cavity, promoting better beam quality [2.4].

![Plot of The heuristic equation for O₂(a) yield required for [I*] = 0.5[I] (optical transparency) as a function of temperature. The O₂(a) yield required to achieve positive gain decreases significantly as temperature is reduced. With cavity temperatures in the range 150-200 K, O₂(a) yield of ~10% is sufficient to produce gain and laser output.](image)

2.2. O₂(a¹Δ) Production

In classic COIL, O₂(a) is generated by a complicated process involving mixing hydrogen peroxide with an alkali metal hydroxide (KOH), to form O₂H⁻ ions, which react with chlorine gas in a two-step process to form ClO₂⁻ ions. These ClO₂⁻ ions dissociate, forming Cl⁻ and the desired singlet delta oxygen O₂(a¹Δ). The net energy released is 355 kJ/mol, with 94 kJ/mol of that energy stored in O₂(a¹Δ) (see Avizonis et al. [2.5] for details). As discussed in Section 1, this method of generation requires use of a significant amount of bulky, hazardous chemicals and therefore presents logistics issues.
Fortunately, O$_2$(a) and O$_2$(b) (singlet oxygen) can be produced by other means, and O$_2$(b) is effectively deactivated to O$_2$(a). Typical (gas-phase) mechanisms are described in Table 2.1: (1) electron impact, (2) UV absorption, (3) ozone photodissociation, (4) recombination of excited atoms, and (5) deactivation of singlet sigma oxygen O$_2$(b) to O$_2$(a).

<table>
<thead>
<tr>
<th>#</th>
<th>Mechanism</th>
<th>Reaction</th>
<th>Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Electron impact</td>
<td>e$^-$ + O$_2$(X) $\rightarrow$ O$_2$(a) + e$^-$</td>
<td>EEDF Dependent</td>
<td>[2.6]</td>
</tr>
<tr>
<td>2</td>
<td>UV absorption</td>
<td>O$_2$(X) + hv $\rightarrow$ O$_2$(b)</td>
<td>Intensity dependent</td>
<td>[2.7]</td>
</tr>
<tr>
<td>3</td>
<td>O$_3$ photodissociation</td>
<td>O$_3$ + hv $\rightarrow$ O$_2$(a,b) + O</td>
<td>Intensity dependent, O$<em>2$(a) $\lambda</em>{\text{threshold}} = 611$ nm, O$<em>2$(b) $\lambda</em>{\text{threshold}} = 463$ nm</td>
<td>[2.8]</td>
</tr>
<tr>
<td>4</td>
<td>Oxygen Atom Recombination</td>
<td>O + O + M $\rightarrow$ O$_2$(a,b) + M</td>
<td>4.5x10$^{-14}$ exp(630/T) [cm$^3$/s]</td>
<td>[2.9]</td>
</tr>
<tr>
<td>5</td>
<td>Singlet Sigma Deactivation</td>
<td>O$_2$(b) + M $\rightarrow$ O$_2$(a,X) + M</td>
<td>8.0x10$^{-14}$, M = O [cm$^3$/s] 3.7x10$^{-17}$, M = O$_2$ [cm$^3$/s] 3.3x10$^{-12}$, M = O$_3$ [cm$^3$/s]</td>
<td>[2.8] [2.10] [2.8]</td>
</tr>
</tbody>
</table>

Therefore, there are other avenues which can be explored for O$_2$(a) production for use in an oxygen-iodine laser system. In ElectricOIL, mechanism 1 in Table 2.1 is exploited, and significant levels of O$_2$(a) are produced in a flowing gaseous discharge. However, due to the use of electric discharge, all of the mechanisms in Table 2.1 (and others) can play a role in O$_2$(a) production. Mechanisms 2 and 3 can occur because of photons produced in the discharge from electronically-excited states. Mechanism 4 is important, because there is significant oxygen dissociation in the discharge. Mechanism 5 is important because significant levels of O$_2$(b) are produced and deactivated to O$_2$(a) by various mechanisms within the discharge and in the discharge afterglow.

Electron impact production of O$_2$(a) becomes further complicated due to the additional electron impact processes which can occur in oxygen discharges. Figure 2.2 describes the various pathways of (electronic) energy through the O$_2$(a$^1\Delta$) state within an electric discharge and in the discharge afterglow. A number of states in addition to O$_2$(a$^1\Delta$) are produced by electron impact: vibrationally-excited O$_2$, O$_2$(b$^1\Sigma$), oxygen atoms, excited oxygen atoms, and ions. Additionally, O$_2$(a$^1\Delta$) is formed by collisions with excited atoms and electron impacts with vibrational levels. Also, O$_2$(b$^1\Sigma$) is deactivated to O$_2$(a$^1\Delta$) by various mechanisms: superelastic collisions, and quenching by oxygen atoms, molecules, and
diluent gas (typically helium). Once $O_2(a^1\Delta)$ is produced, there are several possible deactivation mechanisms: electron impact dissociation, elastic and superelastic collisions creating ground state, $O_2(b^1\Sigma)$, and ions, and quenching by various species in the discharge and afterglow.

![Diagram of various electronic energy pathways through $O_2(a^1\Delta)$]

Figure 2.2. Various electronic energy pathways through $O_2(a^1\Delta)$.

Thus $O_2(a)$ production in gaseous electric discharge is a complex problem, and this is why numerous modeling efforts have been focused on simulation of the discharges for electric oxygen-iodine lasers. The problem of simulating $O_2(a)$ production for use in an oxygen-iodine laser has been worked on by various modelers at the University of Illinois [2.11, 2.12, 2.13], at CU Aerospace [2.1, 2.14, 2.15], at AFRL [2.16] and in Russia [2.17, 2.18]. The various modeling efforts differ in dimensionality and theoretical complexity, but all are in agreement that significant levels of $O_2(a)$ can be produced in an electric discharge, typically in the neighborhood of 30% for optimal conditions. In addition, most have demonstrated decent agreement with experimental trends (especially [2.1, 2.14, 2.15, 2.17, 2.18]).
2.2.1 The Energy Levels of Oxygen

In order to understand the excitation of O$_2$(a) and other species in the ElectricOil discharge, it is helpful to consider the various possible electronic energy states of O$_2$. Figure 2.3 shows the potential energy curves for O$_2^-$, O$_2$, and O$_2^+$ taken from Krupenie [2.19]; this chart describes a variety of ways that electronic and photonic energy can be stored in oxygen: vibrational excitation, electronic excitation, dissociation, ionization, and attachment. The spectroscopic notation of the electronic states shown in Fig. 2.3 is complicated and two different formats are required (one for molecular states and one for atomic states). Both notations are a short-form for description of the electronic configuration of the atom or molecule which describes only the configuration of the outer (excited) electrons, and not the configuration of electrons in inner orbital levels. Since this system of labeling electronic states will be important when discussing the spectroscopic diagnostic techniques used, a brief explanation will be given here.

For atoms, the electronic designation (term symbol) has the form (see Fowles [2.19]):

$$X(2S+1)A_J$$

X is the atom/ion name, $S$ is the spin quantum number, $2S+1$ is the spin multiplicity, $A$ designates the orbital quantum number $L$ ($L = 0, 1, 2...$ for $A = S, P, D...$), and the total angular momentum is $J = L + S$. For example, the ground state of the oxygen atom is designated O($^3$P) which is the short form of O($1s^22s^22p^4$): $A = P$ $\Rightarrow$ $L = 1$, $2S + 1 = 3$ $\Rightarrow$ $S = 1$. $L$ is the sum of angular momentums for 4 electrons in the 3 orbitals of subshell 2p, $L = 1 + 0 - 1 + 1 = 1$. $S$ is the sum of the spins of the 4 electrons in 2p, $S = \frac{1}{2} - \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 1$. In this case, with the subshell more than half full $J = L + S = 2$. In the case that the orbital is less than half full, $J = |L - S|$, and if it is half full $L = 0$ and $J = S$. In Fig. 2.2, $J$ is omitted since it is readily determined from $A$ and $2S + 1$. The first metastable excited state (at 1.967 eV above ground) is designated O($^1$D): $A = D$ $\Rightarrow$ $L = 2$, $2S + 1 = 1$ $\Rightarrow$ $S = 0$. This indicates that the $m_l = -1$ (or +1) orbital in 2p is empty, while the other two are full with the spin of each pair offsetting, and $L = 1 + 0 + 1 + 0 = 2$ (or $L = 0 -1 + 0 - 1 = -2$). The second metastable excited state (at 4.19 eV) is designated O($^1$S): $A = S$ $\Rightarrow$ $L = 0$, $2S + 1 = 1$ $\Rightarrow$ $S = 0$. This indicates that the $m_l = 0$ orbital is empty and $L = 1 - 1 + 1 - 1 = 0$.

For molecules, the electronic designation (term symbol) has the form (see Fowles [2.19], or Herzberg [2.20]):
\[ M(y^{(2S+1)A_{g/u}^{+/−}}) \]

In a similar fashion to the atomic designation, \( M \) is the molecule/ion name, \( S \) is the spin quantum number, \( A \) denotes the orbital angular momentum quantum number \( \Lambda \) (\( \Lambda = 0, 1, 2, \ldots \) for \( A = \Sigma, \Pi, \Delta, \) etc.). Additionally, there is a lower-case or capital letter \( y \) that names the state, and the subscript \( g \) or \( u \) denotes the existence of an inversion center (parity). The \( g \) stands for gerade (which is German for even) and denotes an even wave function, while \( u \) stands for ungerade (German for odd) denotes an odd wave function. There is an additional superscript “+” or “−” added for \( A = \Sigma (\Lambda = 0) \), “+” denoting that there is a symmetry plane containing the internuclear axis, and “−” denoting that there is not. For \( \Lambda > 0 \), this does not apply because there is always a two-fold degeneracy, one state being symmetric and the other being antisymmetric about the reflection. In the remainder of this thesis, molecular states will be designated using the form \( M(y) \) only to denote the state name or \( M \) only if the state is the ground state. For example \( \text{O}_2(a^1\Delta_g) \) will be referred to as \( \text{O}_2(a) \), and \( \text{O}_2(X^3\Sigma_g^-) \) will be referred to as either \( \text{O}_2(X) \) or simply \( \text{O}_2 \).

Optical transitions between various states of oxygen (and of other species) are useful in analyzing the make up of the ElectricOIL discharge plasma and the afterglow. In particular, the transition between \( \text{O}_2(a^1\Delta_g) \) (referred to as \( \text{O}_2(a) \) throughout this work) and \( \text{O}_2(X^3\Sigma_g^-) \) (ground state \( \text{O}_2 \)) is of interest because \( \text{O}_2(a) \) is the precursor which pumps the laser state \( I^* \), and this is monitored using the \( v'' = 0 \) to \( v' = 0 \) band at 1268 nm to determine \([\text{O}_2(a)]\) (see Section 4). Also the transition from \( \text{O}_2(b^1\Sigma_g^+) \) to \( \text{O}_2(X^3\Sigma_g^-) \) is used to determine the flow temperature from the \( v'' = 0 \) to \( v' = 0 \) band at 762 nm, and \([\text{O}_2(b)]\) since a significant percentage of the oxygen exits the discharge in that state. In addition, soft UV emissions from \( \text{O}_2(c^1\Sigma_u^-) \), and \( \text{O}_2(A^3\Sigma_u^+) \) to ground \( \text{O}_2(X^3\Sigma_g^-) \) are used to monitor plasma volume. Electronically excited states of the oxygen atom are also important in the use of actinometry, in particular the pumping of the \( \text{O}(2p^3\Pi) \) ground state to the \( \text{O}(3p^5\Pi) \) and \( \text{O}(3p^3\Pi) \) which then emit at 777 and 844 nm respectively. Understanding of these notations is not crucial, but it is important to consider the various energy levels and the characteristics of the states from which the emissions originate and consider what impact these have on diagnostic techniques and analysis of the laser system. Several questions should be asked: How is the state pumped? What are the various paths by which energy leaves the state
(spontaneous emission, collisional deactivation, further pumping to higher energy levels)?
What is the rate of these other processes? What is the lifetime of the state (i.e. is it a metastable or short-lived)? What state results from the observed emission? Will the state exist in the afterglow or rapidly decay outside of the discharge zone? How much power is deposited into this state, and what happens to that power in the discharge and afterglow?

2.2.2 Cross-sections of Important Excited States

The pumping of various excited states like those shown for oxygen in Fig. 2.2 and 2.3 occurs in ElectricOIL by electron impact, that is

\[ e^- + M \rightarrow M^* + e^- \]

where \( M^* \) denotes an electronically excited state of molecule (or atom) \( M \) at an energy \( \varepsilon_{th} \) above the ground state. The pumping rate of this reaction is modeled as a cross-section interaction with a population energy distribution of electrons. The electron gas is modeled as an electron temperature-dependent continuum of distributed energy while the cross-section is an experimentally-determined probability function having a threshold at the energy level of the excited state. The rate of production of \( O_2^* \) density by direct electron-impact is given by the product \( k_{ij}n_e[M] \) where \( n_e \) is the electron density, and

\[
k_{ij} = \int_{\varepsilon_a}^{\varepsilon_b} \sigma_{ij}(\varepsilon)v(\varepsilon)F(\varepsilon)d\varepsilon
\]

(Eqn. 2.3)

In Eqn. 2.3, \( i \) denotes the initial state (\( O_2 \)) and \( j \) denotes the final state (\( M^* \)) such that \( k_{ij} \) is the rate coefficient for production of state \( j \) from state \( i \), \( \sigma_{ij} \) is the energy-dependent cross-section for the process excitation of \( j \) from \( i \), \( v \) is the electron velocity as a function of electron energy, and \( F(\varepsilon) \) is the normalized electron energy distribution function (\( \int F(\varepsilon)d\varepsilon = 1 \)).
Figure 2.3. Potential energy curves for $O_2^-$, $O_2$, and $O_2^+$ (taken from Krupenie [2.21]).
Figure 2.4 shows Maxwellian electron energy distribution functions (EEDFs) at varied electron temperature plotted along with electron impact cross sections for excitation of ground state O₂ to O₂(a), O₂(b), and dissociation to O(³P) + O(³P) (O(³P) is the oxygen atom ground state). From this it is easy to see that the rate coefficient of each process (Eqn. 2.3) will vary as electron temperature varies, and that the distribution of power into various states will be dependent on EEDF. Low electron temperature will favor low energy processes, while high electron temperatures will favor high energy processes. Assuming the EEDF and a linear interpolation to the cross section data, determination of the production rate of each state is trivial using a numerical integration.

2.2.3. Electron Energy Distribution and Electric Field-to-Gas Density Ratio (E/N)

Since the excitation rates of various states by electron impact are a function of the EEDF, it is necessary to develop a model of the EEDF in order to determine how production rates will vary dependent on plasma parameters, in particular the electric field-to-gas density ratio $E/N$. This parameter essentially determines the electron temperature at which the plasma operates. As $E/N$ increases, the electron temperature $T_e$ (characteristic energy of the electrons) increases, and the energy of the electron gas is redistributed to higher energies. Two approaches are typical, either (1) the Boltzmann equation is solved to determine the
EEDF dependent on the state of the background gas, or (2) a Maxwellian (equilibrium) distribution is assumed for the EEDF allowing for more simplified analysis.

The plasma is better described by the Boltzmann model which incorporates the interaction between electrons and the background gas of the plasma (O₂, He, oxygen atoms, and excited states). This is accomplished by solution of the Boltzmann equation for the number of particles \( f(r,v,t) d^3r d^3v \) inside a phase space volume \( d^3r d^3v \)

\[
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_r f + \frac{\mathbf{F}}{m_e} \cdot \nabla_v f = \frac{\partial f}{\partial t} |_{c} \quad \text{(Eqn. 2.4)}
\]

The left hand side of Eqn. 2.4 is derived by considering the time rate of change of \( f \) due to the flux of particles into the phase space, while the right hand side accounts for the particles which are added to or removed from the phase space volume by collisions (assumed to happen over a very short time scale) [2.22]. In Eqn. 2.4 \( \mathbf{F} \) is the Lorentz force \( q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \). Moments of Eqn. 2.4 can be taken to determine macroscopic conservation equations for mass, momentum, and energy [2.22].

The most simplified version of Eqn. 2.4 is to assume that the electrons are in thermal equilibrium and do not interact with the background gas, such that there are no time variation, no spatial gradients, no accelerations, and no terms due to collisions reducing the equation to \( \frac{\partial f}{\partial t} = 0 \). The solution to this, the Maxwellian distribution for electron velocity is given by [2.22]

\[
f(v) = \left( \frac{m_e}{2\pi kT_e} \right)^{3/2} \exp \left( -\frac{m_e v^2}{2kT_e} \right). \quad \text{(Eqn. 2.5)}
\]

This corresponds to average electron velocity

\[
\bar{v} = \left( \frac{8kT_e}{\pi m_e} \right)^{1/2} \quad \text{(Eqn. 2.6)}
\]

Eqn. 2.5 can be used to determine the normalized distribution as a function of energy

\[
F(\varepsilon) = 4\pi \bar{v}^2 f(v) dv/d\varepsilon = \left( \frac{1}{\varepsilon_k} \right)^{3/2} \left( \frac{4\varepsilon}{\pi \varepsilon_k} \right)^{1/2} \exp \left( -\frac{\varepsilon}{\varepsilon_k} \right) \quad \text{(Eqn. 2.7)}
\]

where \( \varepsilon_k = kT_e \) is the characteristic energy of the Maxwellian distribution function (see [2.23]).
From Eqn. 2.7, it is clear that the pumping of excited states as specified by Eqn. 2.3 will be dependent on the characteristic energy of the EEDF. However, it is unclear what macroscopic parameters will control the EEDF. To determine this, the mean kinetic energy $w_e$ of the electron gas should be considered [2.23]; the time rate of change of $w_e$ is

$$\frac{dw_e}{dt} = p_{el} - \frac{2m_e}{M} v_e n_e \left( \frac{3}{2} (\varepsilon_k - \varepsilon_G) \right) - \sum_j n_j v_{inel} \Delta W_j, \quad p_{el} = \frac{n_e e^2}{m_e v_e} E^2 \quad \text{(Eqn. 2.8)}$$

The first term in Eqn. 2.8 is the rate at which the electric field $E$ transfers energy to the electron gas, the second term accounts for gas heating by elastic collisions (where $\varepsilon_G$ is the characteristic energy of the background gas atoms or molecules), and the third term accounts for the energy lost from the electron gas due to inelastic conditions, $v_{inel}$ being the inelastic collision rate, and $\Delta W_j$ being the energy loss of the inelastic collision (for example $O_2(a)$ excitation, $\Delta W_j = 0.977$ eV). Assuming a steady-state, neglecting the inelastic losses, and defining the collision frequency as the product of the gas density, collisional cross section, and the thermal velocity of the electrons ($v_e = N \sigma_c v_{th}$) results in

$$\varepsilon_k = \varepsilon_G + \frac{M}{3} \left( \frac{e}{m_e \sigma_c v_{th}} \right)^2 \left( \frac{E}{N} \right)^2 \quad \text{(Eqn. 2.9)}$$

Typically, $\varepsilon_G$ will be much smaller than $\varepsilon_k$. Discharge values of $\varepsilon_k$ will be around a few eV, while the discharge gas temperature will be in the range 300-700 K corresponding to (0.026 – 0.06 eV). Therefore $\varepsilon_k$ will be a monotonically increasing function of the parameter $E/N$, the electric field-to-gas density ratio. However, in order to more adequately determine the distribution of electron energy, it is necessary to construct a detailed model similar to that given by Eqn. 2.4 which includes inelastic processes which are neglected in determining Eqn. 2.9.

As described by Palla [2.15], the BLAZE-IV model constructed specifically for modeling ElectricOIL solves the classical two-term spherical harmonic expansion of the Boltzmann equation using a scheme based on the method from Rockwood [2.24]. This formulation allows the modeling of various elastic and inelastic processes by input of experimental cross-section data [2.15]. This non-equilibrium solution has a substantial effect on the EEDF and therefore the electron-impact kinetics. Figure 2.5 shows the normalized EEDFs calculated using BLAZE-V (an upgrade from BLAZE-IV) along with the
Maxwellian distributions at the same characteristic values of $E/N$ ($E/N = 1, 10, \text{and} 20 \text{Td, } 1 \text{Td} = 1 \times 10^{-17} \text{ V-cm}^2$) with (a) only ground state gases, and (b) 20% $O_2(a)$ yield, 2.4% $O_2(b)$ yield, and 7% $O(^3P)$ yield (taken from [2.25]). In Fig. 2.5, the characteristic shape and energy of the EEDF is dominated by the $E/N$ while the distribution of oxygen excited states has a marginal effect which is more substantial for lower values of $E/N$. The general effect of including the non-equilibrium processes is to shift population from the high-energy tail of the EEDF towards lower energy. The inclusion of excited states in the calculation affects the characteristic shape (more significantly at low $E/N$) due to the interplay between a significant population of electrons and excited states at low energies ($O_2(a)$ and $O_2(b)$ levels are 0.977 and 1.627 eV respectively). The result is a dual peak in the EEDF with the second peak of electrons in the region of the thresholds of $O_2(a)$ and $O_2(b)$ due to superelastic collisions with these species. These calculations indicate that $E/N$ of 1-10 Td result in electron temperatures between approximately 0.4 and 2.7 eV, and thus discharges operating in this region should maximize $O_2(a)$ production, since these ranges will allow for a significant population of electrons capable of $O_2(a)$ excitation [2.25].

Figure 2.5. BLAZE-V calculated normalized non-equilibrium EEDFs as a function of $E/N$ assuming (a) zero excited states, and (b) 20% $O_2(a)$ yield, 2.4% $O_2(b)$ yield, and 7% $O(^3P)$ yield. Both cases are compared with equilibrium Maxwellian distributions at the same characteristic energy. The gas mixture is 10:33:0.15 $O_2$:He:NO [2.24].
2.3. \( \text{O}_2(a^1\Delta) \) Saturation

A significant problem in ElectricOIL work is the observed saturation and rollover of \( \text{O}_2(a) \) yield with discharge power input. A desired result for best laser performance would be a discharge in which every watt input to the discharge was converted to 1 watt of power carried by the \( \text{O}_2(a) \) flow, and that every oxygen molecule entering into the discharge region would be exited to the \( \text{O}_2(a) \) state, for this would correspond to a discharge that was optimal in both mass and energy efficiency. However, this is not case, and the deposition of energy into \( \text{O}_2(a) \) is subject to various penalties: elastic collisions (gas heating), vibrational excitation, excitation of other electronic states, and dissociation (see for example Fig. 2.1). Even with these considered, linearity of \( \text{O}_2(a) \) with power might be expected, with some significant fraction of power being deposited into \( \text{O}_2(a) \) and the rest being devoted to other processes. To first approximation this is true, and \( \text{O}_2(a) \) is often pumped linearly with power at low power levels in various discharge configurations.

However, as more significant levels of \( \text{O}_2(a) \) are reached, the influence of superelastic collisions becomes significant and limits \( \text{O}_2(a) \) production. Therefore, as the electrons pump the \( \text{O}_2(a) \) state by the inelastic process, the \( \text{O}_2(a) \) state also returns power to the electron gas by the reverse (superelastic) process.

\[
e^{-} + \text{O}_2(X) \rightarrow \text{O}_2(a) + e^{-} \quad \text{(inelastic)} \quad (\text{R. 2.3})
\]

\[
e^{-} + \text{O}_2(a) \rightarrow \text{O}_2(X) + e^{-} \quad \text{(superelastic)} \quad (\text{R. 2.4})
\]

The cross-section for the superelastic process \( \sigma_{se} \) can be found from the inelastic cross-section \( \sigma_{inel} \) using detailed balance as

\[
\sigma_{se} = \left( \frac{\epsilon + \Delta \epsilon}{\epsilon} \right) \left( \frac{g_X}{g_a} \right) \sigma_{inel} \left( \epsilon + \Delta \epsilon \right). \quad \text{(Eqn. 2.10)}
\]

Parameters \( g_X = 3 \) and \( g_a = 2 \) are the statistical weights (degeneracy) respectively of the \( \text{O}_2(X) \) and \( \text{O}_2(a) \), and \( \Delta \epsilon \) is the threshold of the \( \text{O}_2(X) \rightarrow \text{O}_2(a) \) transition, 0.977 eV. Defining the superelastic cross-section in this way allows for the possibility that electrons at all energies can participate in superelastic collisions. This ensures that the ratio of the probability that an electron will participate in Reaction 2.3 to the probability that it will participate in Reaction 2.4 \( \sigma_{inel} / \sigma_{se} \) is less than unity, and increases with electron energy, approaching a limit at high energy of \( g_a / g_X = 2/3 \) [2.25].
Assuming an equilibrium between $O_2(a)$ and $O_2(X)$, and considering only Reactions 2.3 and 2.4, $O_2(a)/O_2(X)$ will approach the ratio $\frac{\sigma_{\text{inel}}(\varepsilon)}{\sigma_{\text{se}}(\varepsilon)} = \frac{2}{3}$ at high energy. The $O_2(a)$ yield (ignoring other states and dissociation) will approach $\frac{4.05}{2} = 0.4$ (Eqn. 2.11)

and therefore $O_2(a)$ yield is limited by superelastic collisions [2.24].

Equation 2.10 highlights the fundamental “impossibility” of creating greater than 40% $O_2(a)$ in an electric discharge. This simple result is backed up by numerous experimental results in oxygen discharges reporting yields in the range 10 – 32 % (see references from Section 1 [1.14, 1.18-1.23]). However, the realistic limitations on $O_2(a)$ production are more restrictive, and are related to quenching, dissociation and residence time. This can be demonstrated using a simple, time-dependent, constant temperature model of $O_2(a)$ production considering only a few reactions, R. 2.3 and 2.4 along with

$$e^- + O_2(X) \rightarrow 2O + e^- \text{ (dissociation) (R. 2.5)}$$

$$O_2(a) + M \rightarrow O_2(X) + M \text{ (quenching) (R. 2.6)}$$

From Reactions 2.3-2.6, the time rate of change of $n_X = [O_2(X)]$, $n_a = [O_2(a)]$, and $n_O = [O]$ is

$$\frac{dn_X}{dt} = -k_{2.3}n_en_X + k_{2.4}n_en_a - k_{2.5}n_en_X + \sum_q k_{2.6,q}n_a[M]_q \text{ (Eqn. 2.12.a)}$$

$$\frac{dn_a}{dt} = k_{2.3}n_en_X - k_{2.4}n_en_a - \sum_q k_{2.6,q}n_a[M]_q \text{ (Eqn. 2.12.b)}$$

$$\frac{dn_O}{dt} = k_{2.5}n_en_X \text{ (Eqn. 2.12.c)}$$

The rates of Reactions 2.3-2.5 can be determined from cross-section data and an assumed EEDF. Assuming a Maxwellian distribution at $T_e = 2$ eV and the cross-sections shown in Fig. 2.3 in Eqn. 2.3, the computed rates are $k_{2.3} = 4.17 \times 10^{-10}$ cm$^3$/s, $k_{2.4} = 1.02 \times 10^{-9}$ cm$^3$/s, and $k_{2.5} = 2.15 \times 10^{-10}$ cm$^3$/s (considering the 4.5 eV in Fig. 2.4 process only to model dissociation). The rate of the quenching mechanism $k_{2.6,q}$ will be chosen as M-dependent, using rates from [2.14]: 8.2 x10$^{-19}$ cm$^3$/s for $[M] = [O_2(X)]$, 1.7 x10$^{-17}$ cm$^3$/s for $[M] = [O_2(a)]$, and 2.0 x10$^{-16}$ cm$^3$/s for $[M] = [O]$. Therefore the $O_2(a)$ quenching will increase as $O_2(a)$ and O-atoms are produced. Figure 2.6.a shows the time-evolution of $O_2(a)$ yield for the model described by Eqn. 2.12 for two conditions (i) no dissociation, and (ii) with dissociation. In
either case, the yield saturates at ~29% at ~100 ms. The O$_2$(a) density obtained depends on whether or not dissociation mechanism (R. 2.5) is included. In the case without dissociation, the density saturates at ~1.1x10$^{16}$ cm$^{-3}$, while in the case including dissociation, it reaches a maximum near 30 ms and begins to decrease as the level of dissociation increases (increasing quenching and removing ground-state O$_2$). Figure 2.6.b shows the time evolution of O$_2$(a) density as the ratio of the inelastic rate to the superelastic rate varies due to variation of the electron temperature (characteristic energy of the Maxwellian EEDF). The electron temperature has a strong influence on the electron-impact rates, and as $T_e$ increases, the ratio of the dissociation rate to O$_2$(a) excitation rate increases. As electron temperature increases, the slope of O$_2$(a) with time is initially higher because of increased ratio of the inelastic-to-superelastic rate. The O$_2$(a) inelastic-to-superelastic ratio approaches a maximum for high $T_e$, and the dissociation rate continues increasing with increasing $T_e$, resulting in higher quenching of O$_2$(a) as oxygen atoms build up. The simple calculation shown in Fig 2.6 is not accurate considering that it uses a Maxwellian EEDF, and neglects various mechanisms (O$_2$(b) production, 2-body and 3-body O-atom recombination mechanisms, etc.). However, it illustrates the general behavior that O$_2$(a) production will be governed by the characteristic temperature of the EEDF, and influenced significantly by dissociation.

Figure 2.6. Simple model of O$_2$(a) production using Eqn. 2.12: (a) $T_e$ is 2 eV with and without dissociation, (b) $T_e$ varies such that the ratio of the inelastic to superelastic electron impact rates for O$_2$(a) varies and the dissociation rate varies. The electron density is 5x10$^{-10}$ cm$^{-3}$. The flow conditions are 10:33 O$_2$:He at 5 Torr, $T_{gas}$ = 300 K.
The BLAZE model [2.15] allows a more detailed analysis of the O\(_2\)(a) saturation behavior. Figure 2.7 shows the O\(_2\)(a) production efficiency as a function of \(E/N\) for varied O\(_2\)(a) yield in the range of 0% to 35%. The dynamics are similar to those calculated in Fig. 2.6. As O\(_2\)(a) (increases with fixed \(E/N\) or \(T_e\)), the efficiency of O\(_2\)(a) production decreases significantly, approaching zero for high yields. The optimal \(E/N\) for efficient O\(_2\)(a) production increases significantly, by about a factor of 10, as the yield increases from 0% to 35%.

![Figure 2.7. Production efficiency of O\(_2\)(a) versus \(E/N\) as a function of the O\(_2\)(a) yield for 1:4 O\(_2\):He determined using the Blaze Boltzmann model. As O\(_2\)(a) yield increases, the peak in efficiency decreases and shifts to a higher \(E/N\).](image)

2.4. Kinetics in the Discharge Afterglow

ElectricOil post-discharge kinetics have been modeled extensively using the BLAZE models constructed by Palla at CU Aerospace [2.14, 2.15], and similar RF discharges in O\(_2\):He mixture have been modeled by others [2.17, 2.18]. The 1-D BLAZE II model [2.14] was in excellent agreement with post-discharge O\(_2\)(a), O\(_2\)(b), I\(^*\) and gain measurements from Carroll et al. [2.26]. The 1-D BLAZE IV model was in reasonable agreement with experimental results for a 10-cm gap longitudinal capacitive RF discharge [2.15]. The results for various species (O\(_2\)(a), O\(_2\)(b), O-atoms, O\(_3\)) and temperature were similar comparing the model with measurements, but the model under-predicted the effect of NO on O\(_2\)(a) production (although the magnitude was similar within ±20%), under-predicted the O-atom decay and over-predicted the O\(_2\)(b) decay [2.15]. However, the overall agreement was
decent considering (i) unknown kinetics like the branching of \( O_2(b) + O \rightarrow O_2(a,X) + O \) (Mechanism 5 in Table 2.1) and the specifics of kinetics related to NO, (ii) lack of surface reactions in the model, and (iii) dimensionality of the model compared to the non-uniform flow field of the experiment. The addition of O-atom wall recombination would have made the results more agreeable [2.15]. Important trends of the experiment due to NO were well replicated:

1. O-atom decay increased significantly
2. The \( O_2(a) \) production increased significantly
3. The ozone production decreased dramatically

These three effects are related in that O-atoms are depleted by reactions with NO, and the depleted O-atom level leads to decreased \( O_2(a) \) decay from the reaction \( O_2(a) + O_2 + O \rightarrow 2 O_2(X) + O \) and decreased ozone buildup from \( O + O_2 + M \rightarrow O_3 + M \) [2.15]. The BLAZE models produced results which were consistent with measurements of discharge excited state production, and observed behaviors in the downstream (afterglow) kinetics. Thus, they have been used extensively to model ElectricOIL experimental results.

2.4.1. \( O_2(a) \) Quenching by Oxygen Atoms

From the BLAZE modeling of ElectricOIL experimental results, it is obvious that understanding the influence of O-atoms on the system is vital to performance. Without removing oxygen atoms from the system to control quenching mechanisms a viable ElectricOIL would not have been possible [2.26].

In earlier ElectricOIL modeling work at lower pressures, it was established that the two-body quenching of \( O_2(a) \) by O-atoms,

\[
O_2(a) + O \rightarrow O_2(X) + O \quad \text{(2-body quenching)} \quad \text{(R. 2.7)}
\]

was significant, dominating quenching in the afterglow, having a rate of \( k_{2.7} = 2 \times 10^{-16} \text{ cm}^3/\text{s} \) [2.12].

At higher pressures, Braginskiy et al. [2.17.a] found that the 3-body recombination reaction involving \( O_2(a) \),

\[
O_2(a) + O(^3P) + O_2 \rightarrow O(^3P) + 2 O_2(X) \quad \text{(3-body quenching)} \quad \text{(R. 2.8)}
\]

was necessary to properly model the decay found near the discharge exit, determining that the rate of \( k_{2.8} = 1 \times 10^{-32} \text{ cm}^6/\text{s} \) gave best agreement (this rate was also used in BLAZE
modeling [2.14, 2.15]). In high pressure modeling of ElectricOIL experiments, Palla et al. [2.14] found that Reaction 2.8 was the most significant quenching mechanism followed by O$_2$(a) pooling (2O$_2$(a) $\rightarrow$ O$_2$(b) + O$_2$(X)), and then 2-body quenching to O$_2$(X) by atoms (R. 2.7), O$_3$ and O$_2$(a).

**2.4.2. Conversion of O$_2$(b) to O$_2$(a)**

While O-atoms are responsible for significant quenching of O$_2$(a), they also serve to convert O$_2$(b) to O$_2$(a) by the mechanism

$$\text{O}_2(\text{b}) + \text{O}(3\text{P}) \rightarrow \text{O}_2(\text{a}, \text{X}) + \text{O}(3\text{P}) \quad \text{(conversion).}$$  \hspace{2cm} (R. 2.9)

This mechanism has an accepted rate of $k_{2.9} = 8 \times 10^{-14}$ cm$^3$/s [2.8]. A 90% branching to O$_2$(a) in (R. 2.9) is assumed in modeling based on data for various other species which quench O$_2$(b) resulting in high (>0.9) branching to O$_2$(a) [2.8]. This results in a significant amount of the O$_2$(b) produced in the discharge being converted to O$_2$(a) [2.12]. It is responsible for the rapid decrease in O$_2$(b) observed downstream of the discharge. O$_2$(b) is also deactivated to O$_2$(a) by ozone at a fast rate ($3.3 \times 10^{-12}$ cm$^3$/s [2.8]), but this is likely negligible when NO is present and ozone production is suppressed as in most ElectricOIL experiments [2.15].

**2.4.3. I* Quenching by Oxygen Atoms**

Suppression of oxygen atom flow rates by introduction of NO$_X$ (NO and NO$_2$) was necessary due to the fast rate of the quenching reaction

$$\text{I}^* + \text{O} \rightarrow \text{O} + \text{I} \quad \text{(I* quenching).}$$  \hspace{2cm} (R. 2.10)

The reaction rate of $k_{2.10} = 8 \times 10^{-12}$ cm$^3$/s was recently measured by Azyazov et al. [2.27], which is slightly faster than the rate of $3.5 \times 10^{-12}$ cm$^3$/s determined by Carroll et al. [2.26] in work with ElectricOIL. Even with the use of NO to reduce the O-atom flow rate, this mechanism is still responsible for significant loss of the power carried by O$_2$(a) between iodine injection and the laser cavity (see for example [2.14], or more recent modeling results with BLAZE reported by Zimmerman et al. [2.28]).

Another effective means of reducing the flow rate of oxygen atoms is by introduction of a catalytic coating of HgO to the discharge tube walls [2.18]. Rakhimova et al. investigated O$_2$(a) production in small diameter 160 MHz discharges at high pressure in the power deposition range of 100-1000 J/mmol O$_2$ and concluded that similar significant
increases in O$_2$(a) production could be achieved with HgO coating and trace NO (10% or O$_2$) [2.18]. Rakhimova also concluded that trace NO and HgO catalytic coating could be combined to give further improvement [2.18].

2.4.4. I$_2$ Dissociation by Excited States and Oxygen Atoms

Typically, iodine is injected to an oxygen-iodine laser as a molecular vapor. In COIL, the injected iodine is rapidly dissociated by multi-step process with O$_2$(a) or directly by O$_2$(b) generated by O$_2$(a) pooling. The mechanisms and associated rates are

\[
\begin{align*}
I_2 + O_2(b) & \rightarrow O_2 + 2I \quad (k_{2.11} = 2.8 \times 10^{-11} \text{ cm}^3/\text{s}, [2.27]) \quad (R. 2.11) \\
I_2 + O_2(a) & \rightarrow O_2 + I_2^* \quad (k_{2.12} = 7.0 \times 10^{-15} \text{ cm}^3/\text{s}, [2.29]) \quad (R. 2.12) \\
I_2^* + O_2(a) & \rightarrow O_2 + 2I \quad (k_{2.13} = 3.0 \times 10^{-10} \text{ cm}^3/\text{s}, [2.29]) \quad (R. 2.13)
\end{align*}
\]

The presence of significant levels of oxygen atoms introduces another two-step dissociation process for I$_2$,

\[
\begin{align*}
I_2 + O & \rightarrow IO + I \quad (k_{2.14} = 1.4 \times 10^{-10} \text{ cm}^3/\text{s}, [2.30]) \quad (R. 2.14) \\
IO + O & \rightarrow O_2 + I \quad (k_{2.15} = 1.4 \times 10^{-10} \text{ cm}^3/\text{s}, [2.30]) \quad (R. 2.15)
\end{align*}
\]

The rates of this two-step process are fast, and due to the relative densities of O-atoms and O$_2$(b) in ElectricOIL, the two-step process with O-atoms tends to dominate the classic COIL mechanism.

2.5. NO$_X$ Kinetics

The effects observed when NO or NO$_2$ are introduced into the discharge and afterglow are particularly interesting, showing that NO$_X$ can effectively reduce oxygen atom flow rates, and lead to higher O$_2$(a) yields. While the kinetics which lead to the removal of oxygen atoms are well understood from atmospheric science studies [2.31], the influence that NO$_X$ has on O$_2$(a) production within the discharge is convoluted and is likely due to a combination of a variety of mechanisms. These effects will be expanded on in Section 7, but an incomplete list of mechanisms that may be important is given here for purposes of discussion. Three basic mechanisms arise with introduction of NO or NO$_2$:

1. gas kinetic effects which influence O$_2$(a) by removing quenchers (O-atoms and ozone)

2. change in discharge electrodynamics due to lowered ionization potential
(3) improved electron-impact pumping of O$_2$(a) due to conversion of O-atoms to ground state O$_2$

Mechanisms (1) and (2) have been observed in ElectricOIL experiments: (1) has been observed through faster O-atom decay observed with NO added to the discharge [2.15], by the reduction of ozone buildup when NO is added to the discharge [2.15], and by the removal of atoms by titration [2.26]; (2) has been observed by monitoring the decrease in discharge voltage as NO flow rate is increased, but the change in voltage required to maximize the benefit in O$_2$(a) production is very small [2.26]. Mechanism (3) is suspected to have significant influence based on modeling, but experimentally it is difficult to differentiate between this and removal of quenchers. Examining the (spatial) buildup of O$_2$(a) in the discharge in the presence of NO is complicated due to intense NO(C$\rightarrow$A) transitions observed in the NIR which interfere with the 1268-nm emission measurement.

2.6. ElectricOIL Kinetics Discussion

The easy conclusion to be drawn here is that ElectricOIL is a complex kinetic system evidenced by the numerous mechanisms overviewed in this section (which are only a subset of the kinetics in the BLAZE model [2.15]) and the numerous modeling and experimental investigations which have been undertaken. Fortunately, there has been a significant level of historical work done on the measurement of oxygen electron impact cross-sections, and on the various gas-phase kinetics rates associated with oxygen species and iodine, allowing modeling of ElectricOIL mechanisms at a very detailed level. Some key points about ElectricOIL kinetics should be reiterated:

1. O$_2$(a) is produced by electron impact, a non-selective approach which allows energy to be deposited into the flow in a variety of other ways (elastic collisions, vibrational excitation, other electronic states, dissociation).

2. A non-equilibrium Boltzmann code (BLAZE) which solves for the EEDF as a function of $E/N$ is necessary to appropriately model the discharge electron-impact kinetics.

3. O$_2$(a) saturates with power (or residence time in a constant power density); the yield level at which it saturates is determined by the characteristic temperature of the EEDF, and on the influence of O$_2$ dissociation. The theoretical limit specified by the
equilibrium between the inelastic (forward) and superelastic (reverse) electron impact mechanism is 40%.

(4) O$_2$(b) is effectively converted to O$_2$(a).

(5) Oxygen atoms are the primary quencher of O$_2$(a) and rapidly quench I* when iodine is injected, resulting in power carried by O$_2$(a) being lost.

(6) Introducing NO and NO$_2$ to the discharge or afterglow are effective means of removing atoms, and allowing sufficient I* pumping to achieve positive gain and extract laser power. Mercury oxide coatings have also been used effectively to scavenge atoms in oxygen discharges.

(7) While being an effective O$_2$(a) and I* quencher, oxygen atoms also rapidly dissociate I$_2$, a required step in a viable ElectricOIL.

The electrodynamics and kinetics of the ElectricOIL discharge therefore call for a robust diagnostic approach which allows investigations of excited state production and discharge behaviors. From the kinetic and electrodynamic mechanisms discussed here, it is obvious that O-atoms produced in the discharge play a major role in the O$_2$(a) production, and in the transfer of the power carried by O$_2$(a) to atomic iodine for laser extraction. Therefore, methods of measuring O-atoms in the ElectricOIL discharge and afterglow have been devised and applied. Using these O-atom diagnostics, and diagnostics for O$_2$(a) and other excited states, investigations of the discharge characteristics which promote O$_2$(a) production have been made. The knowledge obtained in these investigations allows for development of higher-order modeling capability, and insight into what design choices should be made to improve O$_2$(a) production and the laser output in future ElectricOIL designs.

References


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3. Radio-Frequency Discharge Design and Analysis

The work described in this thesis was conducted using a number of different radio-frequency (RF) power supplies and manual matching networks used to condition the power for various discharge configurations in O₂/He mixtures. Some power supplies were fixed frequency, while others were broadband amplifiers, driven by a wave generator at the desired frequency. Since most early ElectricOIL work with RF was done at a fixed frequency of 13.56 MHz, the initial matching networks were designed specifically for this purpose. As other excitation frequencies were explored, the matching networks were redesigned to match power at the new fixed frequency, or as in the case of the broadband amplifier, the network was redesigned to allow additional flexibility in the circuit such that a single device could be used to match power over a range of frequencies. The laboratory was equipped with a variety of oscilloscopes, current probes, and voltage probes which allowed monitoring of the matching circuit / discharge circuit. This section will summarize the various RF equipment and discharge configurations, and then discuss the theory and analysis involved with matching RF power into the plasma.

3.1. Radio-Frequency Power Supplies and Circuit Monitoring Equipment

A number of RF power supplies and circuit monitoring probes were used in studies of oxygen-helium discharges applied in ElectricOIL. Table 3.1 summarizes the various power supplies used in discharge studies which allow RF power in the range of up to 5 kW, and a variety of excitation frequencies. The fixed frequency supplies weigh in the range of 60 – 100 lbs/kW (27-46 kg/kW).

<table>
<thead>
<tr>
<th>#</th>
<th>Manufacturer / Model</th>
<th>Power Requirements (60 Hz)</th>
<th>Weight [lbs.]</th>
<th>RF Frequency [MHz]</th>
<th>RF Power Range [kW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ENI / OEM-12A</td>
<td>208 VAC, 20 A</td>
<td>126</td>
<td>13.56, fixed</td>
<td>1.25</td>
</tr>
<tr>
<td>2</td>
<td>ENI / OEM-25A</td>
<td>208 VAC, 3-phase, 20 A/phase</td>
<td>225</td>
<td>13.56, fixed</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>ENI / OEM-50</td>
<td>208 VAC, 3-phase, 25 A/phase</td>
<td>375</td>
<td>13.56, fixed</td>
<td>5.0</td>
</tr>
<tr>
<td>4</td>
<td>ENI / A-1000</td>
<td>208 VAC, 3-phase, 22 A/phase</td>
<td>370</td>
<td>0.3-35</td>
<td>~1.0 @ 27 MHz</td>
</tr>
<tr>
<td>5</td>
<td>Comdel / CPS-1001</td>
<td>208 VAC, 3-phase, 6 A/phase</td>
<td>75</td>
<td>60, fixed</td>
<td>1.25</td>
</tr>
</tbody>
</table>
The forward and reverse RF power from the power supply to the matching network circuit was monitored using a pair of Bird Electronics Corporation Thruline Model 43 Watt Meters; a variety of plug-in elements which determine the power and frequency range of these meters were used, allowing 25 W, 50 W, 100 W, 500 W, 1000 W, 2.5 kW, and 5.0 kW ranges in the 2-30 MHz range, and 1000 W range in the 50-125 MHz range. A high power range plug-in was used for the forward power, and a low power range plug-in was used on the reflected power in order to maximize the accuracy of the measurement of power into the matching circuit.

Currents in the matching network were typically monitored using Pearson Electronics Model 411 Wide Band Current Monitors placed in each loop of the circuit. These transformer monitors are placed around a conductor in the circuit, and have a coaxial output which is connected to the high-impedance input of an oscilloscope via a 50 Ω coaxial cable, resulting in a faithful reproduction of the current waveform with a sensitivity of 0.1 V per A. The Model 411 has a small insertion resistance of 2x10^-4 Ω which should be negligible in calculations; the useful frequency range (flat response) of this monitor is 1 Hz to 20 MHz, and therefore it was only useful when analyzing the circuits designed for 13.56 MHz, and in a few other cases investigated where the frequency was less than 20 MHz.

Voltages in the circuit were measured by two means, either using a Tektronix P6015 1000x attenuation high-voltage probe, or a custom-built capacitive pick-up probe which was calibrated to the P6015. The Tektronix P6015 can be used for frequencies from DC up to 75 MHz, and therefore could be used over the entire frequency range of the experiments performed here. The maximum input voltage of the P6015 is reduced at frequencies above 1 MHz, but the derating curves show that the probe is capable of ~5 kV at 13.56 MHz, which is significantly higher than the voltages it was used to measure in the experiments.

3.2. Discharge Configurations

A variety of RF discharge configurations were tested in ElectricOIL development. These configurations include (a) inductively-coupled (electrodeless) -- ICRF, (b) longitudinal capacitively-coupled -- LCCRF, and (c) transverse capacitively-coupled -- TCCRF. A sketch of each type is shown in Figure 3.1. In (a) ICRF, the power is coupled into the flow tube by RF current running through a copper coil wrapped around the circumference of the tube. In
(b) LCCRF, a discharge is formed between two electrodes separated by a gap along the flow tube axis; Fig. 3.1.a demonstrates a hollow cathode design in which aluminum electrodes are sealed into the joints between flow tubes and exposed directly to the gas. It was also possible to construct a LCCRF discharge using two copper straps clamped to the outside of the tube, which adds the tube wall as capacitive ballast along the current path. In (c) TCCRF the electrodes are clamped on either side of the flow axis such that the current path is transverse to the flow direction.

A variety of transverse capacitively-coupled RF (TCCRF) discharges were investigated. The configurations are described in Table 3.2. For reference, the power deposition for 1 kW into the tube volume between the electrodes is shown; the power deposition (W-cm\(^{-3}\)) varies over approximately one order of magnitude for the cases shown. The term “clamshell” is used to describe a set of foil electrodes which conform to the outer wall of the tube. In the circular parallel plate configuration, two flat electrodes are clamped parallel to each other on opposite sides of the flow tube, such that there is a narrow contact line between the electrode and the outer tube wall. In the case of the rectangular parallel plate configuration, the quartz tube has flat walls with a rectangular cross-section, and two flat electrode plates are clamped on top and bottom of the side of the tube cross-section. These three configurations are illustrated in Fig. 3.2.
Table 3.2. Transverse RF discharge geometries.

<table>
<thead>
<tr>
<th>#</th>
<th>Flow Tube, Electrodes Configuration</th>
<th>Maximum Internal Gap [cm]</th>
<th>Internal Volume [cm³]</th>
<th>Wall Thickness [cm]</th>
<th>Power Deposition @ 1 kW [W-cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Circular, “Clamshell”</td>
<td>4.9</td>
<td>479</td>
<td>0.25</td>
<td>2.09</td>
</tr>
<tr>
<td>2</td>
<td>Circular, Parallel Plate</td>
<td>4.9</td>
<td>479</td>
<td>0.25</td>
<td>2.09</td>
</tr>
<tr>
<td>3</td>
<td>Rectangular, Parallel Plate</td>
<td>3.0</td>
<td>465</td>
<td>0.30</td>
<td>2.15</td>
</tr>
<tr>
<td>4</td>
<td>Circular, Parallel Plate</td>
<td>2.0</td>
<td>77.4</td>
<td>0.15</td>
<td>12.9</td>
</tr>
<tr>
<td>5</td>
<td>Circular, Parallel Plate</td>
<td>1.6</td>
<td>51.0</td>
<td>0.15</td>
<td>19.6</td>
</tr>
</tbody>
</table>

Figure 3.2. Cross-sectional sketches of TCCRF discharge configurations investigated for use in ElectricOIL.

3.3. Matching Network Design

The circuit for matching RF power from the source to the discharge varied depending on the desired configuration (inductive, longitudinal capacitive, transverse capacitive) and excitation frequency. The circuit configurations used to match the various discharge configurations are shown in Figure 3.3. The configuration shown in Fig. 3.3.a was used to match inductive discharges, where the inductor coil $L$ is wrapped about the flow tube and excites the gas along its axis. The capacitive RF discharges could be matched with the circuits shown in Fig. 3.3.b-c. The circuit in Fig. 3.3.b is sometimes referred to as a low-pass, LL high-low network. The circuit shown in Fig. 3.3.c is a modified version of the one in Fig. 3.3.b which includes a series inductor and capacitor in parallel with the discharge.
The circuit shown in Fig. 3.3.d is a modified version of the low-pass, LL high-low network which has one coil that is fixed to the variable capacitor $C_1$, while connections for the elements capacitor $C_2$ and the plasma load can be repositioned along the coil. This is especially useful for matching the capacitive discharges at various frequencies. Varying node positions allowed matching at a specific frequency with a specific set of tuning and matching capacitors.

![Figure 3.3.](image)

Figure 3.3. Typical impedance matching network configuration, (a) low-pass PI matching network, (b) low-pass, LL high-low network, (c) low-pass, LL high-low network with second stage in parallel to plasma (d) low-pass, LL high-low network with discretely variable inductor coil.

The purpose of the matching network is to maximize power coupling into the plasma. Maximum power transfer into the circuit will occur when the impedance of the circuit/plasma vessel combination (across the terminals of $C_1$) is equivalent to the internal impedance of the source. Thus, the elements of the matching network must be tuned to create terminal conditions at the electrodes that allow ignition of the plasma, and then retuned to minimize reflected power from the circuit and maintain the plasma.

### 3.3.1. Inductive Discharge Matching

In the case of the inductive discharge (Fig. 3.3.a) the goal is to maximize the power transfer to the plasma from the inductive coil, $L$. This analysis is from Verdeyen [3.1]. The
transfer of power from the coil to the plasma is described by Maxwell’s second equation (the Maxwell-Faraday equation)

\[ \int E_\phi \cdot d\phi = -\frac{\partial}{\partial t} \int B_z \cdot r dr d\phi \]  
(Eqn. 3.1)

The time-varying current in the coil results in a time-varying magnetic field \( B_z \) along the \( z \)-axis of the coil (direction of flow), which induces an electric field \( E_\phi \) along the azimuthal \( \phi \)-axis of the coil.

If the power transfer to the plasma is treated simply as a resistive component to the coil, the analysis of the circuit in Fig. 3.3.a becomes fairly straightforward [3.1]. In this case, the resistance of the coil and the plasma are the only components that accept any real power, and the power coupled into the plasma is simply

\[ P_p = I_L^2 (R - R_0) = P_m - I_L^2 R_0, \]  
(Eqn. 3.2)

where \( I_L \) is the current measured in the coil, \( R \) is the total resistance of the plasma and coil, \( R_0 \) is the ohmic value of the coil resistance, and \( P_m \) is the measured power into the matching network (incident power minus reflected power, \( P_i - P_r \)). This analysis ignores the reactive effects of the coil which couples power to the plasma both capacitively and inductively. Power is coupled capacitively due to the large voltage drop across the coil \( L \); it is this voltage drop which initially ignites the discharge. Since the plasma is a conductor, it acts as a terminal, and the capacitance between the coil and the plasma (due to the air gap and quartz tube) is therefore in parallel with the coil. This effectively increases the inductance of the coil. Power is coupled inductively as in Eqn. 3.1. The plasma acts as a secondary of a transformer in which the coil \( L \) is the primary. The induced magnetic induction from the plasma current is in the opposite direction of the induction from the coil current, and therefore the magnetic flux is effectively decreased due to the plasma. Since the inductance is linear with the magnetic flux, \( L = N \Phi / I \), the coil inductance is effectively reduced by the plasma, which is the opposite of the effect of capacitive coupling. Both of these effects are dependent on the plasma density, and therefore the power deposited. The effect due to inductive coupling will increase with plasma density and therefore dominate at high power, while the effect due to capacitive coupling will dominate at low powers, and decrease as power increases.
Ignoring these reactive effects in the coil, it is possible to make a simple straightforward analysis of the circuit in Fig. 3.3.a, which allows determination of the ranges of matching network capacitors and inductors. The selection of the values for \( L \) and \( C_2 \) will be somewhat arbitrary, and it will be important to choose the proper value of \( C_1 \) that matches the source resistance \( R_s \) to the coil resistance \( R \), and choose the combination of \( L \) and \( C_1 \) such that the reactance of the circuit goes to zero (i.e. the total impedance of the circuit/plasma combination is purely resistive). The impedance across the terminals (a, c) of \( C_1 \) must match the internal impedance of the RF supply \( (R_s = 50 \, \Omega) \). The admittance across the terminals (a, c) is given by

\[
Y_{ac}(\omega) = j\omega C_1 + \left[ R + j\omega L + \left( j\omega C_2 \right)^{-1} \right]^{-1} = G_{ac}(\omega) + jB_{ac}(\omega). \quad \text{(Eqn. 3.3.a)}
\]

For the impedance to be matched, the conductance \( G_{ac} \) must equal the inverse of the source resistance, and the susceptance \( B_{ac} \) must vanish. With some manipulation, Eqn. 3.3.a can be rewritten as

\[
Y_{ac}(\omega) = \frac{R - j\omega C_1[R^2 + (\omega L - (\omega C_2)^{-1})^2] - [\omega L - (\omega C_2)^{-1}]}{R^2 + (\omega L - (\omega C_2)^{-1})^2} = G_{ac}(\omega) + jB_{ac}(\omega). \quad \text{(Eqn. 3.3.b)}
\]

Equating the real and imaginary parts gives two equations which specify the conditions for matching,

\[
G_{ac}(\omega) = \frac{R}{R^2 + (\omega L - (\omega C_2)^{-1})^2} = \frac{1}{R_s}, \quad \text{(Eqn. 3.4.a)}
\]

and

\[
B_{ac}(\omega) = \frac{\omega C_1[R^2 + (\omega L - (\omega C_2)^{-1})^2] - [\omega L - (\omega C_2)^{-1}]}{R^2 + (\omega L - (\omega C_2)^{-1})^2} = 0. \quad \text{(Eqn. 3.5)}
\]

Therefore, setting the susceptance \( B_{ac} \) to zero requires that the term in the brackets \( \{\} \) be set to zero. Equation 3.4 can be rewritten as

\[
\omega L - (\omega C_2)^{-1} = \sqrt{R(R_s - R)} , \quad \text{(Eqn. 3.4.b)}
\]

Plugging this expression into Eqn. 3.5 and solving for \( C_1 \) gives

\[
C_1 = (\omega R_s R)^{-1} \sqrt{R(R_s - R)} . \quad \text{(Eqn. 3.6)}
\]
Therefore, \( R \) must be less than \( R_s \) (for \( C_1 \) to be real), and the value required to match the network will be inversely proportional to frequency. With significant manipulation of the bracketed term in Eqn. 3.5, and introducing the tuning branch resonant frequency \( \omega_2 \), the values of \( L \) and \( C_2 \) can be deduced from

\[
\omega_2^2 = \frac{1}{LC_2} = \omega^2 \left( 1 - \frac{\sqrt{R_s - R}}{\omega L} \right).
\]  

(Eqn. 3.7)

From Eqns. 3.6 and 3.7, the selection of components \( C_1 \), \( C_2 \), and \( L \) will be dependent on the source frequency, and vary dependent on the resistance in the coil which will vary with plasma power deposition \( P_p \). Thus, the network must be designed to allow some flexibility to match varying plasma conditions. Using a 9-turn coil, 3.25” in length, and a diameter of 2”, the inductance of the coil \( L \) (in \( \mu \)H) can be determined from

\[
L = \frac{(nd)^2}{18d + 40l},
\]

(Eqn. 3.8)

where \( n \) is the number of turns, \( d \) is the diameter in inches, and \( l \) is the length in inches, resulting in 1.95 \( \mu \)H (Eqn. 3.8 is taken from [3.2]). With the ohmic resistance of the coil (without plasma) measured as \( R_0 = 1.65 \) \( \Omega \), the values of \( C_1 \) and \( C_2 \) required to match the power into the discharge can be determined. The values of \( C_1 \) and \( C_2 \) required to match the source impedance as a function of frequency are shown in Fig. 3.4 for two conditions (a) \( R = R_0 \), no plasma, and (b) \( R = 10R_0 \), plasma deposited at 90% efficiency. Both capacitances decrease significantly with frequency, and at 13.56 MHz, \( C_1 \) is significantly larger than \( C_2 \) in both cases (a) and (b). Figure 3.5 shows the variation of \( C_1 \) and \( C_2 \) for a fixed frequency of 13.56 MHz for varied resistance in the coil (increasing power deposited into plasma); as the power deposited into the plasma increases, the value of \( C_1 \) is significantly reduced, while the value of \( C_2 \) increases slightly.
3.3.2. Capacitive Discharge Matching

In principle, the matching of the capacitive discharge is similar to that of the inductive setup, in that the goal is to match the impedance of the circuit / plasma vessel combination with the impedance of the source. However, where the plasma vessel was treated as a resistive component of the circuit in series with the tuning capacitor, now it is a reactive and resistive element in parallel with the matching and tuning capacitors. In order to ignite and maintain a discharge it is necessary to add a few elements which compensate for the changes is the discharge vessel configuration. This was accomplished in a variety of ways. The most direct way was as in both Figs. 3.1.b and d, where a coil inductor is added in series with the new plasma branch. The circuit shown in Fig. 3.1.c is a modified version of this in which a series capacitor and inductor were added in parallel with the plasma vessel; this allowed a variable inductance in parallel with the plasma, which helped in matching power when the geometry of the capacitive discharge was changed from longitudinal hollow cathodes (25.4 cm gap) to a shorter gap transverse configuration (1.6 – 5 cm gap) with power coupled capacitively through quartz tube walls. This geometry change effectively results in an increase in the vacuum capacitance of the discharge. This extra capacitance can be balanced in the circuit by a parallel variable inductance, provided by the additional inductor.
L_3 and capacitor C_3 in Fig. 3.1.c. In later work with the smaller gap, smaller electrode area transverse discharges (1.6-1.9 cm internal diameter tubes), the capacitance due to the quartz is greatly reduced, and the “second-stage” in Fig. 3.1.c was not necessary.

To illustrate the matching of power in capacitively-coupled RF discharges (CCRF), an example will be constructed, using the circuit in Fig 3.3.d to match a transverse capacitive configuration (with dielectric material between the electrodes and plasma flow). The plasma vessel can be modeled as depicted in Fig. 3.6, using the (homogeneous) Godyak model (see [3.3]), where the nonlinear capacitive components of the sheaths combine to form a linear capacitive component which is in series with the homogeneous bulk plasma. The bulk plasma itself is modeled as a complex admittance \( Y_p \) given by

\[
Y_p = j \omega \frac{A}{d} \varepsilon_p = j \omega \frac{A}{d} \varepsilon_0 \left[ 1 - \frac{\omega_p^2}{\omega (\omega - j \nu_m)} \right] = j \omega C_0 + \frac{1}{j \omega L_p + R_p},
\]

(Eqn. 3.9)

where \( \varepsilon_p \) is the complex plasma dielectric constant. In the circuit model, the bulk plasma is represented by a series resistance and inductance in parallel with the vacuum capacitance. The parameters \( \omega_p \) and \( \nu_m \) are respectively the plasma frequency and collision frequency, \( A \) is the area of the transverse discharge plates, and \( d \) is the gap between the electrodes \( h \) minus the sheath thickness \( s_0 \). In the transverse case, a capacitor is introduced on either side of the plasma (bulk and sheath) to model the capacitance of the quartz tube walls. As in the inductive example, the only elements that will accept real power are the resistive components of the matching network coils and the plasma. The section of coil that is shorted will be ignored, and the divided portions of the coil will have the inductance as determined by Eqn. 3.8, and the same resistance and inductance per unit length as in the inductive example. The resistive components of the sheaths have been neglected considering the ionic frequency is lower than the excitation frequency (see for example [3.4]).
Figure 3.6. CCRF plasma vessel circuit model. This is based on the Godyak homogeneous capacitive discharge model discussed in [3.3].

\[ C_q = \varepsilon_q \varepsilon_0 \frac{A}{t_q} \]
\[ C_s = \varepsilon_0 \frac{A}{s_0}, \quad s_0 = \frac{I_1}{\varepsilon_0 \omega A} \]
\[ C_0 = \varepsilon_0 \frac{A}{d}, \quad d = h - s_0 \]
\[ L_p = \left( \omega_p^2 C_0 \right)^{-1}, \quad \omega_p^2 = \frac{e^2 n_e}{\varepsilon_0 m_e} \]
\[ R_p = \nu_m L_p \]

- \( A \) := electrode area
- \( h \) := electrode gap
- \( \nu_m \) := collision frequency
- \( \omega_p \) := plasma frequency
- \( \varepsilon_q \) := quartz dielectric constant
- \( t_q \) := quartz thickness
- \( I_1 \) := current amplitude

Figure 3.7. TCCRF discharge and matching network circuit model. The impedance \( Z_V \) represents the plasma vessel circuit shown in Fig. 3.6.
Figure 3.7 illustrates a circuit model for the LL high-low network sketched in Fig. 3.3.d used to match a TCCRF discharge with impedance $Z_V$. A stray capacitance for the circuit denoted $C_{\text{stray}}$ is included. To maximize power transfer from the source to the circuit, the impedance $Z_4$ across terminals $a$ and $b$ must equal the source impedance. The impedances of each branch are given by the relations

$$Z_0 = \left( Z_V^{-1} + j\omega C_{\text{stray}} \right)^{-1}, \quad \text{(Eqn. 3.10.a)}$$

$$Z_1 = Z_0 + R_2 + j\omega L_2, \quad \text{(Eqn. 3.10.b)}$$

$$Z_2 = \left( Z_1^{-1} + j\omega C_2 \right)^{-1}, \quad \text{(Eqn. 3.10.c)}$$

$$Z_3 = Z_2 + R_1 + j\omega L_1, \quad \text{(Eqn. 3.10.d)}$$

$$Z_4 = \left( Z_3^{-1} + j\omega C_1 \right)^{-1}, \quad \text{(Eqn. 3.10.e)}$$

A MATLAB program was constructed to model the circuit in Fig. 3.7 and determine capacitor values for $C_1$ and $C_2$ required to match the circuit to the source with an internal impedance of 50 Ω dependent on excitation frequency, plasma parameters (electron density and pressure), and dimensions of the coil in the circuit which determine $L_1$, $L_2$, $R_1$, and $R_2$. The plasma vessel impedance as a function of plasma electron density is shown in Fig. 3.8 for varied RF excitation frequencies of 13.56, 27.12, and 60 MHz. As electron density increases, the resistive part of the plasma vessel impedance becomes independent of frequency, while the reactive part of the impedance approaches a constant which decreases in magnitude as the frequency increases. So, for high electron density (high plasma frequency), the resistive part becomes dominated by the plasma resistance, while the reactive part becomes dominated by the capacitance of the sheaths and quartz tube walls.
Figure 3.8. The plasma vessel impedance at varied frequency: (a) resistive part, and (b) reactive part. The calculation assumes $\nu_m = 6 \times 10^{10}$ s$^{-1}$, and vessel dimensions of the 3-cm gap configuration #3 in Table 3.2. The plasma is assumed to fill the entire volume.

Figure 3.9 shows the influence of collision frequency on the plasma vessel impedance. The plasma vessel resistance increases as the collision frequency increases. The plasma vessel reactance is independent of pressure at high electron density, but at low electron density the magnitude increases with collision frequency.

Figure 3.9. The plasma vessel impedance for varied collision frequency: (a) resistive part, and (b) reactive part. The calculation assumes $f = 13.56$ MHz and vessel dimensions of the 3-cm gap configuration #3 in Table 3.2. The plasma is assumed to fill the entire volume.
Figure 3.10. Calculated values for capacitor settings required to match discharges with circuit in Fig. 3.7 with varied collision frequency at (a) 13.56 MHz using $L_1 = 0.82 \, \mu H$, $L_2 = 0.30 \, \mu H$, and (b) 60 MHz using $L_1 = 0.67 \, \mu H$, $L_2 = 0.54 \, \mu H$. The calculation assumes $C_{stray} = 50 \, pF$ and vessel dimensions of the 3-cm gap configuration #3 in Table 3.2. The plasma is assumed to fill the entire volume.

Figure 3.10 shows calculated values for $C_1$ and $C_2$ required for matching the source impedance to the plasma network impedance as a function of plasma density and collision frequency at both 13.56 and 60 MHz. The dimensions of the inductor coils are similar to those used in experiment (2.5” diameter, and ~2 turns per inch). The calculated capacitor setting ranges required are similar to those which worked in experiment. The variable-inductor matching network design shown in Fig. 3.1.d and analyzed in Fig. 3.10.a could be adjusted to match discharges with the ENI A1000 supply up to ~30 MHz using the same variable capacitors but smaller inductor values. Work at 60 MHz with the Comdel CPS-1001 required re-designing the network with smaller range capacitors using a similar sized inductor coil.

3.3.4. Matching Network Components

The matching network components which resulted in good performance were air and vacuum capacitors, and custom-built water-cooled inductor coils made from small-diameter copper tubing. For example, the matching network designated MN #1, which was used to match both longitudinal and transverse capacitive discharges, is shown in Fig. 3.11. Table 3.3 shows the ranges of elements used in the various matching network designs.
Table 3.3. Matching network components

<table>
<thead>
<tr>
<th></th>
<th>Inductive</th>
<th>MN #1</th>
<th>MN #2</th>
<th>MN #3</th>
<th>MN #4</th>
<th>MN-60</th>
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<tr>
<td>f [MHz]</td>
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<td>13.56</td>
<td>13.56</td>
<td>variable</td>
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**Capacitors**

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<td>variable</td>
<td>variable</td>
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<td>variable</td>
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<tr>
<td>C1, lower [pF]</td>
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<td>72</td>
<td>72</td>
<td>72</td>
<td>72</td>
<td>9</td>
</tr>
<tr>
<td>C1, upper [pF]</td>
<td>1760</td>
<td>1760</td>
<td>1760</td>
<td>1760</td>
<td>1760</td>
<td>110</td>
</tr>
</tbody>
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</tr>
</thead>
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<td>variable</td>
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<td>variable</td>
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<td>C3, lower [pF]</td>
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<td>5</td>
<td>10</td>
<td>10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>C2, upper [pF]</td>
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<td>125</td>
<td>205</td>
<td>205</td>
<td>125</td>
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**Inductors**

<table>
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<th>fixed</th>
<th>variable</th>
<th>variable</th>
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<tbody>
<tr>
<td><em>Coil</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Length [in.]</td>
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<td>4.50</td>
<td>3.25</td>
<td>5.50</td>
<td>4.50</td>
<td>3.50</td>
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<tr>
<td>Diameter [in.]</td>
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<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Turns, Total</td>
<td>#</td>
<td>9</td>
<td>10.5</td>
<td>9</td>
<td>11.5</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>(typ.)</td>
<td>(typ.)</td>
<td>(typ.)</td>
<td>(typ.)</td>
<td>(typ.)</td>
<td>(typ.)</td>
</tr>
<tr>
<td>Turns, L1</td>
<td>turns</td>
<td>9</td>
<td>5.5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>L1 [μH]</td>
<td>1.95</td>
<td>1.36</td>
<td>1.33</td>
<td>1.11</td>
<td>1.08</td>
<td>0.35</td>
</tr>
</tbody>
</table>

|                | turns  | n / a | 5     | 4      | 2      | 2      |
| Turns, L2      |       |       |       |       |       |       |
| L2 [μH]        | 1.20   | 0.97  | 0.300 | 0.29   | 0.29   | 0.29   |

Figure 3.11. MN #1 matching network used to match 13.56 MHz capacitive discharges. C1 is a 4-bank 12-440 pF per bank air capacitor (right of center), and C2 is a 5-125 pF vacuum capacitor (left of center). The copper, water-cooled coil is 10.5 turns, 4.5” long, and has a diameter of 2.5”. Power is fed to the matching network by the N-type coax connector at the lower right. One end of the inductor attaches to a post on the high-voltage (top) of the matching capacitor C1, and it attaches to the high voltage side of the tuning capacitor C3 at 5.5 turns. The other end of the coil attaches to a brass rod which is fed through the case wall. One electrode is attached via a wire lead to the brass rod, while the other is grounded to the case. Three Pearson Model 411 current monitors are mounted in the circuit, one before the coil, and two after. If the second-stage is used with this circuit, it is attached between the monitors. A capacitive voltage probe is mounted at the feedthru between the coil and the case wall.
3.4. Matching Network Power Efficiency Analysis

Within the matching network, there are significant losses due to the resistance of circuit components. While the circuit model introduced in Section 3.3 allows understanding of what circuit configurations are required for matching as parameters which influence the plasma vessel impedance vary (electron density, collision frequency, excitation frequency, dielectric thickness), it is difficult to use this to adequately model the behavior of a real discharge and determine the efficiency with which power is deposited into the discharge. It is better to make direct measurements of currents and voltages within the circuit, and determine the losses. An analysis of power coupling into LCCRF discharge and a detailed computation of the discharge $E/N$ based on circuit voltage and current measurements was given by Woodard [3.5]. Here, a simple analysis of power deposition into a TCCRF discharge is discussed.

Figure 3.12 shows efficiency of power coupled to the discharge vessel calculated from current and voltage measurements in MN#1 with the add-on circuit (see Fig. 3.3.c). The efficiency is given by

$$\frac{P_p}{RF_{sys}} = \frac{P_i - P_r - I_{L1}^2R_{L1} - I_{L2}^2R_{L2} - I_{L3}^2R_{L3}}{RF_{sys}}, \quad \text{(Eqn. 3.11)}$$

where $I_L^2R_L$ is the average power loss in each coil, $I_L$ is the rms value of the current in the coil and $R_L$ is the series resistance of the coil. In Fig 3.12, the discharge operates in 2 modes: a normal mode where voltage is constant as current increases with increasing plasma volume on the plates, and an abnormal mode where voltage increases as current increases and the plasma is confined to the volume between the plates. In the normal mode the efficiency is low at low current, and increases with current. In the abnormal mode, the efficiency is relatively constant in the range of 92-95%. The behavior in Fig. 3.12 is characteristic of other RF configurations.
3.5. Radio-Frequency Discharge Design Summary

As shown in this section, the available RF equipment made it possible to investigate a variety of discharge configurations. These discharges were rated on their capability of producing O$_2$(a) flow rate, in both efficiency and magnitude. Many configurations of RF, microwave, pulser-sustainer, and hybrid (RF and DC) discharges were investigated and compared. After these comparisons, transverse capacitively-coupled RF (TCCRF) discharges were chosen for detailed study and application to future ElectricOIL versions. Where possible, it will be demonstrated (in the proceeding sections) that TCCRF matched performance or out-performed other configurations in certain regimes. However, it is important to realize that the investigations of TCCRF for high pressure, high O$_2$ flow-rate operation were considerably more extensive than with other configurations. It is possible that carefully designed versions of other configurations (ICRF, LCCRF, microwave, pulser-sustainer, etc.) could also perform well in the high pressure, high O$_2$ flow-rate regime. TCCRF was chosen due to it having reliable O$_2$(a) production performance over a range of pressures, and its robustness due to both the availability of well-manufactured commercial RF power supplies, and the ease of designing matching circuits for various configurations (geometry and excitation frequency) as described in this section.
References

[3.1] Verdeyen, J. T., personal communication and written notes
4. ElectricOIL Optical Diagnostics Suite

In this section, the optical diagnostics and diagnostic techniques used to investigate ElectricOIL will be overviewed. These diagnostics take advantage of the emission or absorption characteristics of various gas species in the flow in order to determine species concentrations. The discussion will begin with various species which are monitored using emission spectroscopy such as singlet oxygen \([O_2(a)]\) and \([O_2(b)]\), followed by species monitored using absorption spectroscopy \([I_2]\), \([O_3]\), and \([I^*]-0.5[I]\). Then, diagnostic techniques for measuring oxygen atom concentrations will be overviewed including airglow techniques based on the chemiluminescent recombination of oxygen atoms with nitric oxide, and the trace argon actinometry (TAA) spectrometry which monitors the relative intensities of excited oxygen atom and argon lines within an active discharge.

4.1. Emission Spectroscopy Diagnostics

A number of species in the ElectricOIL system can be monitored using emission spectroscopy at various locations in the system: within the discharge, in the discharge effluent, in the iodine injection/mixing zone, or in the laser cavity region. Knowledge of lifetimes of these species and the optical setup of the diagnostic used to interrogate the flow allow the measured radiation from a species to be related to the concentration of that species in the flow (absolute intensity). A list of excited states monitored in ElectricOIL studies at the UIUC High-Energy Laser Laboratory is shown in Table 4.1; the notation describing each transition are common notations used in the literature.

The NIR (near-infrared) measurements of \(O_2(a)\) at 1268 nm, \(I^*\) at 1315 nm, and \(NO(C)\) at 1224 nm were performed using Princeton Instruments/Acton Optical Multi-channel Analyzers (OMA). For the various experiments described in this work, two different systems were used: (1) OMA #1, a 512 element (linear) InGaAs array OMA-V coupled to a 150-mm focal length spectrometer with a 600 g/mm grating blazed at 1 \(\mu\)m, and (2) OMA #2, a 1024-element (linear) InGaAs array OMA-V coupled to a 0.3-m focal length spectrometer with both a 600 g/mm and 1200 g/mm grating blazed at 1.2 \(\mu\)m (turret mounted). The change from the first system to the second was made in order to improve the resolution of the \(O_2(a)\) spectra at 1268 nm such that it could be used to deduce the flow temperature (however, this capability has not been applied as of this work).
Table 4.1. Various atomic and molecular excited state emissions monitored in ElectricOIL work.

<table>
<thead>
<tr>
<th>Atom or Molecule</th>
<th>Excited State</th>
<th>Energy Level [eV]</th>
<th>Transition</th>
<th>Emission Wavelength (Observed) [nm]</th>
<th>Pumping Mechanism</th>
<th>Used in determining</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>O₂(a,Δ)</td>
<td>0.977</td>
<td>a → X</td>
<td>1268</td>
<td>Electron impact</td>
<td>[O₂(a)]</td>
</tr>
<tr>
<td>O₂</td>
<td>O₂(b,Σ)</td>
<td>1.63</td>
<td>b → X</td>
<td>762</td>
<td>Electron impact</td>
<td>[O₂(b)]</td>
</tr>
<tr>
<td>O₂</td>
<td>O₂(c,Σ)</td>
<td>4.5</td>
<td>c → X</td>
<td>404.7</td>
<td>Electron impact</td>
<td>Plasma volume</td>
</tr>
<tr>
<td>O₂</td>
<td>A³Σ</td>
<td>4.48</td>
<td>A → X</td>
<td>404.7</td>
<td>Electron impact</td>
<td>Plasma volume</td>
</tr>
<tr>
<td>O</td>
<td>O(P)</td>
<td>10.74</td>
<td>3p ³P → 3s ³S</td>
<td>777</td>
<td>Electron impact, UV</td>
<td>[O] (Actinometry)</td>
</tr>
<tr>
<td>O</td>
<td>O(P)</td>
<td>10.99</td>
<td>3p ³P → 3s ³S</td>
<td>844</td>
<td>Electron impact</td>
<td>[O] (Actinometry)</td>
</tr>
<tr>
<td>NO</td>
<td>NO(C)</td>
<td>6.47</td>
<td>C → A</td>
<td>1224</td>
<td>Electron impact</td>
<td>[NO(C)], UV</td>
</tr>
<tr>
<td>I₂</td>
<td>I₂(B)</td>
<td>1.94</td>
<td>B → X</td>
<td>576</td>
<td>Laser-induced Fluorescence (LIF)</td>
<td>Dissociation fraction using LIF</td>
</tr>
<tr>
<td>I</td>
<td>I(2P1/2)</td>
<td>0.943</td>
<td>2P1/2 → 2P3/2</td>
<td>1315</td>
<td>Resonant energy transfer with O₂(a)</td>
<td>[I*]</td>
</tr>
<tr>
<td>Ar</td>
<td>Ar(2p₃)</td>
<td>13.48</td>
<td>2p₃ → 1s₂</td>
<td>750.4</td>
<td>Electron impact</td>
<td>[O] (Actinometry)</td>
</tr>
<tr>
<td>Ar</td>
<td>Ar(2p₂)</td>
<td>13.27</td>
<td>2p₂ → 1s₄</td>
<td>751.5</td>
<td>Electron impact</td>
<td>[O] (Actinometry)</td>
</tr>
</tbody>
</table>

An Apogee E47 CCD camera coupled to a Roper Scientific/Acton Research 150-mm spectrometer with a 1200 g/mm grating blazed at 750 nm was used to measure the ro-vibrational emission of O₂(b) at 762 nm (from which flow temperature was determined using the method described by Carroll et al. [4.1.]), as well as the emissions of excited atomic oxygen at 777 nm, and excited argon at 750.4 and 751.5 nm which are used in the argon actinometry technique to determine oxygen atom concentration. A Santa Barbara Instruments Group CCD with an Acton 150-mm spectrometer was also used to measure O₂(b), and to monitor laser-induced fluorescence (LIF) of I₂ for dissociation measurements (the I₂ transitions were observed with the monochrometer centered at 576 nm).

Various emissions were also monitored using an Ocean Optics NIR USB 4000 miniature fiber-optic spectrometer which was set up with a 1200 g/mm grating blazed at 750 nm, having a spectral range of 713-985 nm. This diagnostic was useful in simultaneously monitoring various atomic oxygen and argon lines in this range for use in the argon actinometry technique, and in methods of deducing electron temperature (E/N) by comparing line intensities.

The spectrometer/detector combinations were fiber coupled to the diagnostic volume using either Oriel model #77538 glass fiber bundles or ThorLabs 600 µm x 5 m single-core multimode fibers, typically collecting with a bare fiber end.
4.1.1. $O_2(a^1\Delta)$ Emission at 1268 nm

Besides the measurements of gain and laser power out of the ElectricOIL, the most important measurement is that of the density of $O_2(a)$. This measurement determines how efficiently the discharge technique stores power into $O_2(a)$ which serves as the energy reservoir in the system, having a long lifetime of 75 minutes for an isolated molecule [4.2] (the lifetime is about an order of magnitude shorter in an atmosphere of oxygen). Thus, a number of the experiments were focused on the measurement of the $O_2(a \rightarrow X, v' = 0, v'' = 0)$ band emitting at 1268 nm, and the calibration of the measured intensity to the $O_2(a)$ density [$O_2(a)$].

A few sample spectra are shown in Figure 4.1; four cases are shown, spectra from both OMA #1 and #2, showing cases with and without the background airglow due to O-NO recombination. This broadband glow emits from UV to the IR and must be removed from the measured spectra in order to determine the integral counts of the $O_2(a)$ emission at 1268 nm. Fortunately, the O-NO recombination glow has a linear behavior over this range, and can be easily removed by porting the spectral data from the WinSpec32 [4.3] software to Microsoft Excel, and running a macro which removes the O-NO glow [4.4]. Once the spectra has been properly base-lined, the emission at 1268 nm can be integrated and related to the density by

$$[O_2(a)] = F_{cal} \sum_i \frac{c_i \Delta \lambda_i}{\Delta t}$$

(Eqn. 4.1)

where $i$ is the array element number, $\Delta \lambda$ is the resolved wavelength width of the array element, $c_i$ is the counts on element $i$, $\Delta t$ is the exposure time, and $F_{cal}$ is the calibration factor which accounts for the emission rate of $O_2(a)$, and the optical efficiency of the collection of emitted photons from the flow volume.
Figure 4.1. Sample O₂(a) spectra at 1268 nm without and with O-NO airglow present: (a) using OMA#1 (3:16 O₂:He, 20 Torr, 400 W RF), and (b) using OMA#2 (10:33 O₂:He, 16 Torr, 800 W RF). The linear airglow must be removed from the spectra to determine the counts due to the O₂(a) emission. The OMA#2 setup offers better resolution of the spectra having twice the spectrometer focal length, and twice the number of elements on the array.

\( F_{cal} \) can be determined in one of two ways:

**Method #1:** Absolute intensity calibration using a broadband light source

**Method #2:** Determining [O₂(a)] from the temperature-dependent equilibrium between O₂(a) and I*

In the first case (absolute intensity calibration), the collection/detector system used to measure O₂(a) emissions is compared to a broadband lamp of known spectral irradiance (W/nm/steradian). The light collected by the detector viewing this source is compared with the light collected in the flow volume, giving a relative spectral irradiance of the flow volume due to the species of interest, and this is related to the species density.

In the second case (the O₂(a)-I* equilibrium method), [O₂(a)] is determined by measurement of gain ([I*]-0.5[I]), I₂ flow rate, I₂ dissociation fraction, and temperature using the equilibrium rate \( K_{eq} \) (Eqn. 2.2, \([I^*]/[I] = K_{eq}(T)[O_2(a)]/[O_2(X)]\)). \([I^*]/[I]\) is determined readily from gain, I₂ flow rate, and dissociation fraction. If the temperature is known, and equilibrium can be assumed, \([O_2(a)]/[O_2(X)]\) can be determined. \( F_{cal} \) is found by dividing the [O₂(a)] determined from the equilibrium measurement by the integral count rate (bracketed term in Eqn. 4.1). An experiment which uses this method to determine O₂(a) yield is described in Appendix A. Method #2 was applied in the studies discussed in this thesis.
4.1.2. $O_2(b^1\Sigma)$ Emission at 762 nm and deducing flow temperature

Another important molecular oxygen state in ElectricOIL study is $O_2(b)$, another metastable of oxygen at an energy of 1.63 eV. This state has a lifetime of ~11 minutes and its ($\nu' = 0$, $\nu'' = 0$) band emits in the NIR at 762 nm [4.2], and is useful in determining the gas flow temperature within the discharge, and in the discharge effluent, when the density and therefore intensity of the emission is high enough to get a good signal to noise ratio on the measured spectra. A detailed computational modeling of the ro-vibrational spectra of $O_2(b \rightarrow X)$ as a function of temperature and resolution was described by Woodard [4.5]. Typically, a simplified model of the spectra was used in which the temperature was deduced from the ratio of two peaks which are due to the combined influence of the P and Q branch of the emission. The formula for using the peaks with rotational quantum numbers $J_1 = 6$ and $J_2 = 16$ is given by

$$kT \ [cm^{-1}] = \frac{B(J_2(J_2 + 1) - J_1(J_1 + 1))}{\ln \left( \frac{C_R \frac{I_1}{I_2}}{2J_2 + 2.75 \over 2J_1 + 2.75} \right)} = \frac{320}{\ln \left( \frac{2.25C_R \frac{I_1}{I_2}}{J_2(J_2 + 1) - J_1(J_1 + 1)} \right)} \quad (Eqn. 4.2)$$

where $B = 1.391 \ cm^{-1}$ is the rotational constant for oxygen, $I_x$ is the intensity of the emission with quantum number $J_x$, and $C_R = 0.955$ is a constant which accounts for the resolution of the spectra [4.5]. Figure 4.2 shows the spectra of $O_2(b)$ emission at 762 nm, $O_2(b, \nu' = 0) \rightarrow O_2(X, \nu'' = 0)$, at two flow temperatures, 402 K, and 667 K. Note that as the temperature increases, the R branch ($\Delta J = +1$) redistributes to lower wavelengths, while the P ($\Delta J = -1$) and Q ($\Delta J = 0$) branches redistribute to higher wavelengths.
Figure 4.2. Sample $O_2(b, v = 0) \rightarrow O_2(X, v = 0)$ spectra at 762 nm for varied flow temperature. As the flow temperature increases the R-branch ($\lambda < 762$ nm) redistributes to lower wavelength, while the P and Q branches redistribute ($\lambda > 762$ nm) to higher wavelengths. The R-branch is poorly resolved, but the emissions from the combined P and Q branches can be modeled as a function of temperature and resolution in order to extract temperature from the scans shown. Typically, the simplified model shown as Eqn. 4.2 (Woodard [4.5]), which compares only two $J$ rotational quantum numbers, was used in place of the detailed computation.

4.1.3. Herzberg I and II Bands, $O_2(c,A \rightarrow X)$ filtered at 404.7 nm

In order to study the plasma volume, it was necessary to measure excited states with short lifetimes outside of the discharge, such that the emissions of these species could be assumed proportional to electron density. The Herzberg Bands in oxygen are a good candidate for this purpose, considering that they are excited by electron impact (by relatively high energy electrons), have short lifetimes (decaying rapidly outside the discharge), and emit in the violet where they can be easily detected with a digital camera.

The measurement of the Herzberg I and II band groups [4.6] in $O_2$ was accomplished using a Nikon D70 with narrowband 404.7 nm filter placed in the optical path. The filter has a 11-nm bandwidth (399-410 nm), which allows capture of two sets of excited $O_2$ emissions, $O_2(c^1\Sigma \rightarrow X^3\Sigma)$ : $(v',v'') = (1,6), (3,7), (5,8), (6,8), (8,9), (10,10), (11,10)$, and $O_2(A^3\Sigma \rightarrow X^3\Sigma)$ : $(v',v'') = (0,7), (2,8), (5,8), (4,9)$. The filtered camera was set up to view TCCRF discharge configuration #3 (3 cm gap) in two ways: (1) with the optical axis perpendicular to the grounded plate, such that the emission from 0.125” holes in the plate could be collected, and (2) with the optical axis perpendicular to the transverse gap between the plates, such that the transverse structure could be observed. Typical 404.7 nm emission data with the camera optical axis perpendicular to the grounded plate is shown in Fig. 4.3 for a case in which the discharge excitation is uniform.
4.1.4. NO(C $\rightarrow$ A) Emissions in the NIR

The introduction of NO to the discharge results in the production of electronically-excited NO states which emit in the NIR. These emissions cause a major problem in ElectricOIL work because, within the discharge, they dwarf the O$_2$(a) emission, with intensity ratios on the order of 20:1, even with O$_2$:NO of 100:1. Therefore, with trace amounts of NO in the discharge, which tend to improve O$_2$(a) production, it is impossible to make accurate measurements of the 1268 nm O$_2$(a) signal within the discharge, and determine what effect NO has on the character of O$_2$(a) production in the discharge. Figure 4.4 is a sample spectra centered at 1268 nm taken within an active discharge, showing the two NO transitions to lower and higher wavelength. The O$_2$(a) emission appears as a small “blip” on the wings of the two NO emissions. Even when using a filter for the O$_2$(a) emission, it is difficult to determine which portion of the spectra comes from O$_2$(a), and which is from the wings of the NO emissions.

Although the NO(C $\rightarrow$ A) emissions cause problems for measuring O$_2$(a) density within the discharge, they can be useful for studying the discharge dynamics. The NO(C)
state at 6.47 eV can be formed either by electron impact (by electrons of significantly higher energy than those required to excite O$_2$(a)), or by inverse pre-dissociation (recombination of N and O atoms). The 1224 nm emission results in the NO(A) state at 5.45 eV. NO(A) and NO(C) emit in the UV to NO(X) (ground state) with bands in the range 190-340 nm (see for example Groth [4.7]). Thus the pumping of NO in the discharge results in a UV source (high energy photons). These states have recently been observed (along with O$_2$(a)) in NIR measurements of the upper atmosphere of Venus [4.8] which concluded that the C$\rightarrow$A transition accounted for 0.32 branching of the total emission rate from NO(C) (sum of C$\rightarrow$A and C$\rightarrow$X); the earlier work by Groth results in a similar branching ratio of 0.38 [4.7]. The presence of the UV emission from NO excited states is evident by the violet glow observed in the quartz when NO is added to the discharge [4.9]. The energetic UV photons resulting from the NO(A, C) states are of interest for various reasons: pumping of atomic oxygen states, break down of ozone, etc. In this work, the NO(C$\rightarrow$A) emission decreased when the plasma density was decreased (volume increased for constant power), while the O$_2$(a) production improved; this seems to indicate a significant change in the electron energy distribution (a lowering of electron temperature). The energy stored in the NO(C) state will be quantified using 1224 nm measurements in Section 7 where it will be established that despite the large intensity, the energy associated with the UV emissions is small.

Figure 4.4. Sample OMA spectra with NO in the flow, one taken inside the discharge, and one taken downstream of the discharge (~71 cm). The flow conditions were 3:16:0.15 mmol/s O$_2$:He:NO, 12.5 Torr, with 450 W RF. The peak near 1268 nm is similar in either case, but the presence of molecular emissions in NO complicates data reduction, even when filtering techniques are used. When NO is added, the 1268 nm emission of O$_2$(a) is dwarfed by the emissions of NO(C) within the discharge. The excited NO states deactivate rapidly downstream of the discharge, allowing a clean spectra which can be integrated and related to O$_2$(a) density.
4.1.5. Laser-Induced Fluorescence of I\textsubscript{2}

A vital oxygen-iodine laser diagnostic is laser-induced fluorescence of I\textsubscript{2}. When applied correctly, this technique can be used to determine the dissociation fraction of I\textsubscript{2} after its injection into the flow, downstream of the discharge. This is especially useful when using Yield Calibration Method #2 (see section 4.1.1), where it is necessary to have knowledge of the total iodine atom density ([I\textsuperscript{*}]+[I]). In this method, a 514-nm Ar-Ion laser is used to excite I\textsubscript{2}(B) which then emits at various higher wavelengths (lower energies). By holding the laser source constant, and monitoring the I\textsubscript{2}(B) emission at some wavelength, the relative change in [I\textsubscript{2}] density due to some varied parameter, such as discharge power level or NO flow rate can be determined. Typically, the fluorescence of I\textsubscript{2}(B) can be detected simply using a filtered photo-multiplier tube (PMT). However, in ElectricOIL work with NO in the flow, the O-NO recombination emission (O + NO $\rightarrow$ NO\textsubscript{2}* $\rightarrow$ NO\textsubscript{2} + h\nu) influences the PMT signal, and it is instead better to use a spectrometer to monitor the I\textsubscript{2}(B) signal, such that the I\textsubscript{2}(B) emission structure can be differentiated from the broadband NO\textsubscript{2}* glow. Figure 4.5 shows some sample spectra from application of this method to determine I\textsubscript{2} dissociation.

![Figure 4.5. Sample spectra of I\textsubscript{2}(B) used to determine I\textsubscript{2} dissociation fraction. With the discharge off, but 514-nm Ar-Ion laser on, the I\textsubscript{2}(B) structure is observed. When a discharge containing NO and producing oxygen atoms is engaged, a significant broadband glow due to NO\textsubscript{2}* is observed, and the I\textsubscript{2}(B) structure is eliminated. When the Ar-Ion laser is turned off, (discharge remains on), the NO\textsubscript{2}* background remains. A few emission peaks in the laser-induced I\textsubscript{2}(B) structure are labeled: 44$\rightarrow$9 at 568 nm, 44$\rightarrow$11 at 583 nm, 44$\rightarrow$12 at 589 nm, 44$\rightarrow$13 at 596 nm.](image)
4.2. Absorption Spectroscopy Diagnostics

Absorption spectroscopy is used in ElectricOIL work to measure the densities of I\textsubscript{2} and O\textsubscript{3}, and to measure the gain proportional to [I*]-0.5[I]. All of the absorption diagnostics used were developed by Physical Sciences, Inc. (PSI) in Andover, MA, specifically for use in COIL and ElectricOIL work. The aspects of these diagnostics and their application to ElectricOIL are described here.

4.2.1. PSI Microabsorbance Diagnostics for I\textsubscript{2} and O\textsubscript{3}

Two high-sensitivity beam absorption diagnostics \[4.10\] were developed by PSI to measure [I\textsubscript{2}] and [O\textsubscript{3}]. Both diagnostics operate on the basic principle of Beer’s law

\[ I = I_0 \exp(-\sigma NL), \text{ or } N = \frac{\ln(I_0/I)}{\sigma L}, \]  

(Eqn. 4.3)

where \( N \) is the density of the absorber, \( \sigma \) is the absorption cross-section, \( L \) is the path-length of the absorbed beam, \( I_0 \) is the beam intensity without the absorber, and \( I \) is the intensity with the absorber. In order to remove common-mode noise from the light sources, and reduce long-term signal drift due to thermal effects, the PSI diagnostics monitor a reference beam which is split off from the primary beam before it passes through the absorber volume, and the intensities \( I \) and \( I_0 \) in Eqn. 4.3 are replaced with the ratio of the intensities of the beam passing through the absorber chamber and the reference beam with and without the absorber present \( R \) and \( R_0 \) \[4.10\]. The ozone diagnostic uses collimated light from a mercury pen lamp filtered at 254 nm. The iodine diagnostic uses collimated light from a blue diode filtered at 488 nm. The absorption cross-sections for I\textsubscript{2} and O\textsubscript{3} at these wavelengths respectively are 1.63\times10^{-18} \text{ cm}^2 and 1.147\times10^{-17} \text{ cm}^2 respectively. The dual-beam detection with ultra-sensitive, high-precision electrometer circuit enables measurement of absorbances, \( \ln(I_0/I) \), of less than 10^{-5} \[4.10\]. For a 5 cm optical path, this corresponds to minimum detection limits of [I\textsubscript{2}] = 1.2\times10^{12} \text{ cm}^{-3}, and [O\textsubscript{3}] = 1.7\times10^{11} \text{ cm}^{-3}. These detection limits can be influenced by electro-magnetic interference (EMI) from the discharge \[4.10\], but in practice the actual detector limits were adequate for use in measuring the density levels of [I\textsubscript{2}] and [O\textsubscript{3}] in ElectricOIL.

When using these Microabsorbance diagnostics, it is important to consider the various emissions from the discharge region. Care must be taken to avoid the influence of various
bands on the detectors. Although these detectors are filtered at the appropriate wavelength, there are bands which interfere with analysis of each probe beam. For instance, the broadband O-NO airglow coincides with the diode source at 488 nm, while the NO(A→X) UV emission bands coincide with the mercury lamp emissions at 254 nm. Therefore, these emissions must be considered when setting up the experiment and analyzing the data. In practice, the O-NO glow is not a significant issue because the signal is very weak compared to the diode probe beam, but the UV emissions from the discharge have caused significant problems with measuring ozone absorption, especially when NO is introduced in the discharge.

4.2.2. PSI Gain Diagnostic (Ver. 3)

Obviously, the most important measurement in analyzing a laser system is that of the gain, a measure of the population inversion from which laser power can be extracted. In analysis of various versions of ElectricOIL, a PSI iodine gain diagnostic is used, which applies tunable diode laser spectroscopy (TDLS) on the I(2P1/2) → I(2P3/2) (3,4) hyperfine transition at 1315 nm [4.11]. The diode laser output is scanned over the absorption feature, and the average of several sweeps is recorded. The resulting signal can be used to determine the peak gain (in cm⁻¹ or %-cm⁻¹) and the width of the signal can be used to measure the temperature (given an appropriate temperature-dependent model of the signal). A sample measurement is shown in Fig. 4.6.a for a flow at 661 K; Fig. 4.6.b shows a comparison of temperatures obtained using the PSI gain diagnostic, and temperatures determined from the spectra of O₂(b). The two methods are in decent agreement considering the differences in the diagnostic technique. The gain measurement represents an average of the temperature running along the probe beam’s axis which is perpendicular to the flow axis and passes through the centerline of the flow tube. The temperature measurement from the O₂(b) spectral intensity is more heavily influenced by emitters in the viewing volume closest to the fiber face (the influence goes as 1/r²), and therefore is biased towards the temperature of the flow near the wall. Therefore, given that the flow is hotter near the centerline, the O₂(b) temperature should be less than the gain profile temperature which represents a more balance average.
4.3. Airglow Techniques for Oxygen Atom Measurement

Measurement of the broadband emission due to O-NO recombination \( (O + NO \rightarrow NO_2^* \rightarrow NO_2 + hv) \) has been used in ElectricOIL to determine the concentration of oxygen atoms produced in the discharge. Typically this broadband glow was monitored at its peak using a Hamamatsu R955 photo-multiplier tube (PMT) filtered at 580 nm. However, it was also possible to monitor the broadband glow with other diagnostics, for instance one of the NIR spectrometers. There are two different O-NO airglow techniques which have been applied to measure atoms: (1) The Kaufman NO\(_2\) titration technique [4.12], and (2) the Piper airglow intensity calibration technique [4.13]. Both of these methods will be described here. A key factor, especially in applying the Piper method [4.13] to ElectricOIL work is the airglow temperature dependence which will be discussed first.

4.3.1. Temperature Dependence of O-NO Airglow

The intensity of the NO\(_2^*\) emission can be expressed as

\[
I_{NO_2^*} = k_{AG}(T) \cdot [O] \cdot [NO]
\]

(Eqn. 4.4)

In this expression, \( k_{AG}(T) \) is the temperature dependent emission rate, which also is third-body dependent (M-dependent). Clyne and Thrush [4.14, 4.15] produced a detailed work which determined the temperature dependence of the airglow emission due to the chemiluminescence from O-NO recombination for M = O\(_2\) to be \( T^{-3+/-0.8} \) over the temperature...
range 200-300 K, which is equivalent to an exponential form of \( \exp(1500\pm400/RT) \). The
temperature dependence was evaluated at higher temperature by Hartunian et al. (see
Kaufman [4.15]); that work reported two forms \( T^{1.55} \), and \( \exp(2200/RT) \) for \( M = O_2 \). Parkes
(see Kaufman [4.15]) reported a two parameter fit of \( T^m \exp(-300/RT) \) where \( m = 2.50 \) for \( M = O_2 \), and 2.65 for He and Ar for a temperature range of 170-370 K.

The above temperature dependencies are not in full agreement, and were performed at
lower and higher ranges than found downstream of typical ElectricOIL discharges (300-700 K). Also, the background gas in ElectricOIL is typically an O₂:He mixture. In order to
determine the temperature dependence, O-NO recombination measurements and Ar
actinometry measurements were taken downstream of an ElectricOIL discharge in a low
power secondary discharge and compared. The Ar actinometry secondary discharge
technique developed by Braginsky [4.16] was applied. From these measurements, the best
agreement between the two methods was found using a dependence of \( T^{-1.5} \) for \( k_{AG} \).
Therefore, this temperature dependence has been used in ElectriOIL work when applying
airglow techniques for measuring oxygen atoms. Figure 4.7 shows the temperature
dependence of the airglow intensity from various sources in the literature, along with the rate
determined from comparison of actinometry and O-NO recombination in ElectricOIL
analysis. The result obtained from ElectricOIL work is similar to the high-temperature result
from Hartunian et al., and in decent agreement with the exponential form obtained by Clyne
and Thrush at low temperature. The Parkes fit does not compare well to the other data if
applied at high temperature, but the work with various M-gases indicates that \( M = O_2 \) and \( M = He \) were fairly similar. Figure 4.8 shows Ar actinometry and NO₂* airglow data which
showed best agreement using \( T^{-1.5} \) for \( k_{AG} \).
4.3.2. The Kaufman NO₂ Titration Technique

One technique which uses measurement of NO₂* emission from O-NO recombination is the Kaufman titration technique [4.12]. In this method, the oxygen atom flow rate is determined by measuring the NO₂ titration flow rate required to extinguish the airglow. A photo-multiplier tube (PMT) is used to measure the air afterglow emission from the Reactions 4.1 [4.12]

\[
O + NO \rightarrow NO_2^*, \quad k_{4.1.a} = 2.5 \times 10^{-17} \text{ cm}^3/\text{s}, \text{ slow} \quad (R. \ 4.1.a)
\]
\[
NO_2^* \rightarrow NO_2 + h\nu, \quad k_{4.1.b} = 5.54 \times 10^{-20} \text{ cm}^3/\text{s} \quad (R. \ 4.1.b)
\]
as NO₂ is added to the flow. The NO for this reaction is rapidly produced by the reaction

\[
O + NO_2 \rightarrow O_2 + NO, \quad k_{4.2} = 6.5 \times 10^{-12} e^{(120/T)} \text{ cm}^3/\text{s}, \text{ fast} \quad (R. \ 4.2)
\]
which is highly exothermic (1.995 eV) and may result in O₂(X), O₂(a), or O₂(b) [4.17]. The atoms are depleted by Reaction 4.2 and by three-body recombination. Reactions 4.3.a and 4.3.b respectively are published rates [4.17] for air (applied to oxygen) and argon (applied to helium).

\[
O + NO + O_2 \rightarrow NO_2 + O_2, \quad k_{4.3.a} = 4.68 \times 10^{-28} T^{-1.5} \text{ cm}^6/\text{s} \quad (R. \ 4.3.a)
\]
\[
O + NO + He \rightarrow NO_2 + He, \quad k_{4.3.b} = 2.08 \times 10^{-28} T^{-1.41} \text{ cm}^6/\text{s} \quad (R. \ 4.3.b)
\]
As NO₂ is increased, the [NO] increases while [O] decreases by Reaction 4.2. In Kaufman’s experiment [4.12], it was observed that the NO₂* airglow had a parabolic behavior with NO₂ flow rate, having a maximum intensity at half the extinguishing point. This was because at low pressure conditions, Reaction 4.2 dominated the kinetics, and as NO₂ increased, [O] decreased proportionally, while [NO] increased proportionally. Therefore, the measured airglow intensity which is proportional to [O][NO], was parabolic in nature, because it was a product of a linearly increasing function and a linearly decreasing function. Kaufman’s data [4.12] is plotted in Fig. 4.9. For these conditions, the intensity of NO₂* can be modeled analytically (Verdeyen [4.19]) as a function of injected [NO₂] and position along the flow axis \( z \) having the form

\[
I \propto \frac{[O][NO]}{[O]_0} = r(1 - r) \left( \frac{1 - e^{-(1-r)x}}{(1 - re^{-(1-r)x})^2} \right), \quad r = \frac{[NO_2]_0}{[O]_0}, \quad x = \frac{k_{4.2}[O]_0 z}{u_f} \quad \text{(Eqn. 4.5)}
\]

This model is plotted in Fig. 4.10 for varying values of \( x = f(z) \). As \( x \) increases, the analytical model approaches Kaufman’s result. This titration technique works well at low pressure because the peak intensity lies at the half the extinguishing point, corresponding to half of the oxygen atom flow rate. Thus the NO₂ flow rate for peak intensity is determined, and twice this flow rate is the oxygen atom flow rate. However, this technique becomes complicated by recombination mechanisms (Reactions 4.3a and b) when applied to fast flow at higher pressure [4.18], and a more detailed model must be devised in order to deduce sensible results from the technique.
A detailed computational modeling of NO\textsubscript{2} mixing with the effluent of a discharge in O\textsubscript{2}/He mixture was performed by Rakhimova et al. [4.20]. Fluent was used to model an NO\textsubscript{2} titration result from ElectricOIL work (Zimmerman et al. [4.18]) and also compared the data with an analytical model which accounted for recombination mechanisms. The Fluent model and analytical model were in good agreement, and both agreed well with the behavior observed in the experimental case from ElectricOIL work; Rakhimova’s analytical model for the airglow intensity which includes recombination is

\[
I \propto [O][NO] = [\text{NO}_2]_0 ([O]_0 - [\text{NO}_2]_0) \exp(-2 \cdot k \cdot M \cdot [\text{NO}_2]_0 \cdot t) \quad \text{(Eqn. 4.6)}
\]

Where [ ]\textsubscript{0} denotes input density, \( t \) is the transport time between the injector and the detector, and \( k \cdot M \) is a combined recombination rate \( k \cdot M = k_{4.3a}(\sum [O_2(X)] + [O_2(a)] + [O]) + k_{4.3b}[\text{He}] \). This model also gives the parabolic behavior seen in Kaufman’s data for \( 2 \cdot k \cdot M \cdot [\text{NO}_2]_0 \cdot t \ll 1 \), which is not the case for typical ElectricOIL conditions but also gives good agreement with ElectricOIL high pressure data. The key result to be drawn from this analysis is that the NO\textsubscript{2} flow rate for peak NO\textsubscript{2}* intensity observed does not correspond to half the oxygen atom flow.
rate for high pressure conditions and that the NO$_2$ flow rate at which the glow extinguishes at the detector is well correlated to the initial oxygen atom flow rate with proper modeling of the titration kinetics. Therefore, it is best to model the NO$_2$ titration analytically for fast, high-pressure ElectricOIL flows.

4.3.3. The Piper Calibrated O-NO Recombination Emission Technique

A second technique which uses the NO$_2^*$ emission due to O-NO recombination is the Piper calibrated emission NO titration technique [4.13]. In this technique the rate $k_{AG}$ is determined experimentally, and then [O] can be determined experimentally from Eqn. 4.4, or

$$[O] = \frac{I_{NO2^*}}{k_{AG}(T) \cdot [NO]} \quad \text{(Eqn. 4.7)}$$

where $I_{NO2^*}$ is the current monitored on the PMT, and $k_{AG}$ can be determined by an NO titration experiment [4.13]. The magnitude of $k_{AG}$ was determined by NO titration of N atoms from a N$_2$/Ar discharge source [4.13, 4.18]. The technique follows this procedure: (1) the power on the discharge is held constant, producing a “constant” flow of nitrogen atoms; (2) at some downstream location, NO is injected incrementally; (3) a filtered PMT downstream of NO injection measures the afterglow emission produced by excited nitrogen formed by 3-body recombination,

$$\text{N}_2(B) \rightarrow \text{N}_2 + h\nu \quad \text{(green glow)} \quad \text{(R. 4.4)}$$

and the air afterglow emission from Reaction 4.1 (yellow glow). The titration of nitrogen atoms occurs by the fast reaction

$$\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} \quad \text{(R. 4.5)}$$

which also produces oxygen atoms to create the air afterglow from Reaction 4.1. The kinetics of the titration are described in Table 4.2. With increasing NO flow rate, the point at which the green glow is extinguished gives the concentration of nitrogen atoms produced by the discharge. From that point on, the oxygen atom concentration produced by Reaction 4.5 is invariant with NO, and a calibration factor for the PMT can be determined by Eqn. 4.8.

$$k_{AG} = \frac{1}{[O]_0} \frac{dI_{NO2^*}}{d[NO]} \quad \text{(Eqn. 4.8)}$$
Here, $[O]_0$ is the concentration determined from the nitrogen titration endpoint (green glow extinguished), and $d I_{NO2^*} / d[NO]$ is determined from the slope of yellow airglow with increased NO flow beyond the endpoint.

**Table 4.2. A description of the Piper air-glow method calibration.**

<table>
<thead>
<tr>
<th>State</th>
<th>Condition</th>
<th>Description</th>
<th>Behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[N] \gg [NO]$</td>
<td>NO is limiting reagent</td>
<td>$[O]$ is identical to injected [NO], yellow glow created by Reaction 4.4</td>
<td>Green glow linearly proportional to $[N]^2$</td>
</tr>
<tr>
<td>$[N] = [NO]$</td>
<td>N-atom titration endpoint</td>
<td>Endpoint determines $[N]$ produced by discharge</td>
<td>Green glow extinguished</td>
</tr>
<tr>
<td>$[N] &lt;&lt; [NO]$</td>
<td>N is limiting reagent</td>
<td>$[N]$ completely converted to $[O]$, $[O]$ is invariant with $[NO]$, green afterglow created by Reaction 4.1</td>
<td>Yellow glow linearly proportional to $[NO]$</td>
</tr>
</tbody>
</table>

Figure 4.11 shows the PMT data for NO titration downstream of a 40 W microwave discharge in a mixture of 8.8 % N$_2$ in Ar at 8.4 Torr. The NO$_2^*$ glow must be corrected for three-body and wall recombination (assuming constant temperature) using

$$I_{cor} = I_{obs} e^{\alpha t}, \quad \text{where} \quad \alpha = 2 \sum_{M} k_M [NO][M] + k_{wall}.$$  

(Eqn. 4.9)

where $t$ is the flow time between injection and the observation points, $I_{cor}$ is the corrected intensity, $I_{obs}$ is the observed intensity, $k_{wall}$ is the wall recombination rate, and the first term in $\alpha$ is the sum of three-body rates, with the factor of 2 coming from the assumed fast reaction with NO$_2$ which is formed by the three-body processes. Once $k_{AG}$ is determined using the corrected intensity slope, an airglow temperature must be included as discussed in Section 4.3.1. Applied to oxygen discharge effluent, the atomic oxygen flow rate is found using Eqn. 4.7 with $[NO]$, $I_{NO2^*}$ and temperature as known inputs.

The calibration process for this technique is fairly complicated, but if the same calibrated viewing volume (diagnostic flow channel) is used to analyze output from an ElectricOIL discharge concept which contains a known flow rate of NO, and temperature measurement from O$_2$(b) spectra, the data collection and reduction is straightforward, and consistent results are found with little effort. The primary issue with the method is the temperature dependence, which as seen in Figure 4.7 varies substantially over the range of typical ElectricOIL discharges (300-700K); The temperature dependence which worked best when comparing airglow and actinometry results in ElectricOIL work of $T^{-1.5}$ was in good agreement with the rates shown in the literature [4.14, 4.15]. There in an M-effect [4.15]; the
influence of this was not well-established in this work, but the effect of this is assumed to be small compared to the temperature dependence based on the work by Parkes [4.15].

It is also assumed that the NO flowing through the discharge is not dissociated. This assumption is made considering the dissociation level of NO (5.3 eV) compared to the discharge electron temperature, and quick recombination downstream of the discharge (no airglow measurements were made in an active discharge). If the NO is partially dissociated in the discharge effluent, this would mean that the actual oxygen atom densities are higher than those determined. No specific work has been done to determine if there is significant NO dissociation, but there has not been any evidence of excited nitrogen atoms downstream of the discharge (for instance the atomic nitrogen line at 1247 nm which would be visible near the O₂(a) spectra), and modeling of the discharge with BLAZE-IV [4.21] indicates that the NO dissociation is negligible.

![Figure 4.11. PMT signals for air afterglow titration using microwave discharge in Ar:N₂ mixture. The flow is 8.8% N₂ in Ar diluent at 8.4 Torr, and the microwave power level is 40 W.](image)

**4.4. Trace Argon Actinometry Technique for Oxygen Atom Measurement**

One technique which was useful in measuring oxygen atom concentrations in ElectricOIL was trace argon actinometry (TAA). In this technique a small amount of argon gas is added to the flow within a discharge containing oxygen atoms. Then, the ratio of the emission of excited oxygen I(O*) to the emission of excited argon I(Ar*) is measured and used to deduce the oxygen atom density. A calibration factor between the emission ratio
I(O\(^*\))/I(Ar\(^*\)) and the density ratio \([O]/[Ar]\) is determined either from comparison to another technique (ex. O-NO airglow), or through modeling of the excited state pumping. Since the density of argon is known, \([O]\) is determined being proportional to the product \([Ar]\{I(O^*)/I(Ar^*)\} \).

This technique was applied in two ways in ElectricOIL work: (1) used in the primary discharge to measure the buildup of oxygen atoms, and (2) used in a low power secondary discharge downstream of the primary discharge in order to measure oxygen atom decay, and to compare to airglow methods (O-NO recombination, NO\(_2\) titration). This subsection will cover the basic theory, discuss the corrections that must be made in order to apply TAA to moderate pressure, discuss the use of TAA in a secondary discharge (Braginsky method), and then discuss optical methods for determining \(E/N\) (electric field-to-gas density ratio) which controls the pumping of excited states and is vital in calibrating TAA results.

### 4.4.1. Basic Theory of Actinometry

There is a substantial amount of literature available concerning the application of trace-gas actinometry to the measurement of species concentrations in various discharges. Coburn and Chen [4.22] originally applied trace argon actinometry (TAA) to the study of etching plasmas where they were interested in studying the etching rate of silicon by fluorine atoms in CF\(_4\)/O\(_2\) plasmas. Prior to their work, there had been a rough correlation made between the excited fluorine emission at 703.7 nm and the etching rate, but it had also been shown experimentally that the excitation efficiency of the F level responsible for the 703.7 nm emission decreased as the ratio of O\(_2\)/CF\(_4\) increased [4.22]. This occurred because the fraction of species which were electronically excited to the optically emitting excited state changed dependent on the electron energy distribution function, which varied due to the change in O\(_2\)/CF\(_4\). Coburn and Chen found that when they introduced a trace amount of argon gas to the CF\(_4\) + O\(_2\) plasma the variation in the Ar emission at 750.4 nm with O\(_2\)/CF\(_4\) matched the variation in excitation efficiency of the fluorine emission at 703.7 nm found by others [4.22]. Because the electronic energy level of the Ar state responsible for the 750.4 nm emission (~13.5 eV) was similar to the electronic energy level of the F atom state responsible for the 703.7 nm emission (~14.5 eV), they made the assumption that the excitation efficiencies were similar for the two states and that the ratio between the two
would be independent of plasma parameters (electron distribution function). The simple model applied was

\[ I_X = k_X [X] \eta_X \]  
(Eqn. 4.10)

where \( I_X \) is the optical-emission intensity from species X, \([X]\) is the density of species X in the ground state, \( \eta_X \) is the excitation efficiency of the state responsible for \( I_X \), and \( k_X \) is a proportionality constant accounting for optical collection efficiency. Using this model of intensities, and assuming equivalent pumping efficiencies, they used the model

\[ [F] = K \frac{I_{704}}{I_{750}} [Ar]. \]  
(Eqn. 4.11)

In Eqn. 4.11, the intensity ratio \( I_{704} / I_{750} \) was measured, the density of Ar was known, and \( K \) is a constant (assumed) independent of discharge parameters.

In their experiment, Coburn and Chen found that \( I_{750} \) was linear with Ar concentration up to about 5% while \( I_{704} \) remained constant, which indicated that the trace argon did not significantly affect the energy distribution for the energy range of interest [4.22]. Using the TAA method in Eqn. 4.11, they were able to determine that the highest density of F atoms occurred at ~20% \( \text{O}_2 \) (for constant total flow rate, constant power input); beyond this point the density of F atoms decreased linearly, as the \( \text{CF}_4 \) donor density decreased inversely proportional to \( \text{O}_2 \). Use of argon gas as an “actinometer” in Coburn and Chen’s experiment allowed the decrease in pumping efficiency of the F emitting state with change in mixture to be accounted for in the relative determination of \([F]\). They also found that \( I_{750} \) (Ar* intensity) and \([F]\) had the same (sublinear) dependence on RF power, which was expected as both are created by a single electron process having similar energy thresholds (\( e^- + \text{CF}_4 \rightarrow \text{CF}_3 + F + e^- \), at 12 eV, and \( e^- + \text{Ar} \rightarrow \text{Ar}^* + e^- \) at 13.5 eV) [4.22].

The work shown by Coburn and Chen [4.22] can be easily extended to the detection of oxygen atoms in discharges containing oxygen. Walkup et al. [4.23] tested the validity of actinometry to detect oxygen atoms in a \( \text{CF}_4 + \text{O}_2 \) etching plasma, comparing it to two-photon absorption laser-induced fluorescence (TALIF) measurements. The plasma analyzed contained 2-15% atomic oxygen and significant increase over this range was observed upon addition of \( \text{CF}_4 \) to pure \( \text{O}_2 \), this being attributed to increase in electron density with \( \text{CF}_4 \) and not gas-phase chemistry [4.23]. The experiment monitored the intensities of the 777 nm emission from \( \text{O}(3p^3\text{P}) \) and the 844 nm emission from \( \text{O}(3p^3\text{P}) \), taking the ratio of these to...
the 750.4 nm emission of argon. Walkup et al. [4.23] determined that for the conditions used, both direct excitation and dissociative excitation played important roles in the pumping of the O(3p^5P) and O(3p^3P) states,

\[ e^- + O \rightarrow O^* + e^- \quad \text{(direct)} \]

and

\[ e^- + O_2 \rightarrow O^* + O + e^- \quad \text{(dissociative)}. \]

This is a major issue when applying actinometry, because it is necessary for the direct process to dominate in order to find the proportionality

\[ \frac{[O]}{[Ar]} \propto \frac{I_{0^*}}{I_{Ar^*}}. \quad \text{(Eqn. 4.12)} \]

Walkup et al. found that this effect of dissociative excitation was not negligible in cases where O_2/CF_4 ratio was high, but found excellent agreement among \( I_{777}/I_{750} \), \( I_{844}/I_{750} \), and the TALIF result below 85% O_2 [4.23]. The effect was more pronounced when using the 777 nm emission, because the direct excitation cross-section for O(3p^5P) decreases rapidly at high electron energies while the dissociative excitation cross-section is flat. The effect of dissociative excitation was confirmed in the experiment by the broadening of the lines at 844 nm in pure O\_2 which was reduced when 15% CF\_4 was introduced to the mixture and the oxygen atom concentration was increased [4.23]. However, for the conditions of the experiment, \( I_{844}/I_{750} \) was in good qualitative agreement with the TALIF result, while \( I_{777}/I_{750} \) was only in good agreement for less than 85% O\_2 in the O\_2/CF\_4 mixture where oxygen dissociation was high. From Walkup et al., two criteria were established in order for direct excitation to dominate [4.23]:

1. the discharge must be strongly excited such that \([O]/[O_2] > 5\%\), or
2. the direct excitation cross-section must be much larger than the dissociative excitation cross-section as in the case of the 844 nm emission, but not necessarily the 777 nm emission (ex. if \( E/N \) is large).

4.4.2. Actinometry Applied to Moderate Pressure Oxygen Discharges

The application of the method becomes more complex at higher pressures (Coburn and Chen worked in the 30-50 mTorr range and Walkup et al. worked in the 25-500 mTorr range). This is because the quenching rates of excited species by the background gases
become significant compared to the pumping rate of the excited species by the electrons in the discharge. Pagnon et al. applied a modified argon actinometry technique to the positive column of DC glow discharges in oxygen in the pressure range of range 0.36-2 Torr which accounted for the quenching effects of the background gas [4.24]. This work also applied a Boltzmann EEDF solver (similar to the one used in BLAZE modeling) in order to model the pumping of excited states using cross-section data for direct and dissociative excitation. This model was chosen for analysis of the atom production in moderate pressure ElectricOil discharges [4.18, 4.25].

In this technique, the intensity of an emitting state \( X^* \) is related to the ground state concentration \([X]\) by

\[
I_{X^*} = C_{\text{det}}(X^*) \cdot \left( \frac{\hbar \nu_{ij} A_{ij} k_e n_e}{\sum_k A_{ik} + \sum_m k_m [Q_m]} \right) \cdot [X] = C_{\text{det}}(X^*) \cdot \{K_X\} \cdot [X], \quad \text{(Eqn. 4.13)}
\]

where \( C_{\text{det}}(X^*) \) is the detector efficiency for the emission, \( \hbar \nu_{ij} \) is the photon energy of the emission, \( A_{ij} \) is the Einstein spontaneous emission rate for the emission, \( k_e \) is the electronic excitation rate of the initial state, \( n_e \) is the electron density, \( \Sigma A_{ik} \) is the sum of spontaneous emission rates out of the initial state, \([Q_m]\) is the density of initial state quencher \( m \), and \( k_m \) is the quenching rate of the initial state by quencher \( m \). Using this model of the intensity, it is possible to deduce the oxygen atom concentration by flowing trace amounts of argon gas in the discharge and comparing the emissions of excited states of argon and atomic oxygen. The emissions monitored in this analysis were the 777-nm emission of atomic oxygen \( \text{O}(5\text{P}) \), the 750.4-nm emission of excited argon \( \text{Ar}(2\text{p}_1) \), and the 751.5-nm emission of excited argon \( \text{Ar}(2\text{p}_5) \). Using Eqn. 4.13 to formulate the intensities, the atomic oxygen concentration can be determined from

\[
[O] = K_{\text{Ar}/O} \cdot [\text{Ar}] \cdot \frac{I_{777}}{I_{750}}, \quad K_{\text{Ar}/O} = \frac{K_{\text{Ar}}}{K_O}. \quad \text{(Eqn. 4.14)}
\]

The parameter \( K_{\text{Ar}/O} \) in Eqn. 4.14 must be determined either through comparison to another method (ex. airglow measurements) or by modeling the pumping (cross-section and EEDF) and quenching of each state as in Eqn. 4.13. The parameters required for Eqn. 4.13 and the corresponding references are summarized in Table 4.3; the detector efficiencies are assumed to be equal. For the conditions studied in this paper, the quenching terms are significant
compared to the spontaneous decay $A_{ij}$ for both Ar* and O* (which was not the case for Pagnon et al. [4.24]); however, the quenching by helium is negligible compared to quenching by molecular oxygen. The estimated values for quenching rates are based on measurements for similar quenching reactions available in the literature. Francis [4.26] showed that the quenching of Ar(2p$_1$) and Ar(2p$_3$) were similar for Ar, CH$_4$ and C$_2$H$_2$ used as a buffer gas. Various data in the literature [4.27] showed quenching of excited oxygen atom states in He to be a few orders of magnitude slower than in O$_2$. The E/N (electric field-to-gas density ratio) dependent rates are found using a Boltzmann solver for the EEDF (electron energy distribution function) in the desired (O$_2$:He) mixture, and integrating the referenced cross-section with that EEDF and the electron velocity to determine the pumping rate. Katsch et al. [4.30] found that the validity of the 777 to 750 nm line ratio to measure oxygen atoms was influenced by three behaviors: (1) dissociative excitation channel ($e + O_2 \rightarrow O(^5P) + O + e$), (2) secondary electron effects ($\gamma$-mode processes, high energy electrons emitted from the walls), and (3) excitation of O($^5P$) by electron impact with O$_2$(a) ($e + O_2$(a) $\rightarrow O(^5P) + O + e$). All three of these effects could be an issue in the systems studied here, dependent on the operating conditions. However, the discharges studied here with actinometry have fairly low electron temperature (~2 eV), where the dissociative channel should not be significant; also the impact of secondary electrons on the actinometry measurement is expected to be small, considering that the measurements shown here were taken in discharges where the intensity was approximately uniform through the gap (homogeneous discharge). The excitation of O($^5P$) by dissociation of metastable O$_2$(a) was not considered, but could be important considering the fairly high fractions of O$_2$(a) obtained in the discharge (a typical value would be [O$_2$(a)]/N $\sim$ 0.035).

Table 4.3. Parameters used to determine $K_{ArO}$ in Eqn 4.14. The $M = [O_2]$ quenching rates are those used by both Katsch [4.30] and Pagnon [4.2] (originally reported by Dagdigian).

<table>
<thead>
<tr>
<th>Emission</th>
<th>O$^*$(777-nm)</th>
<th>Ar$^*$(750.4-nm)</th>
<th>Ar$^*$(751.5-nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{ij}$ [s$^{-1}$]</td>
<td>3.69x10$^3$, [4.27]</td>
<td>4.45x10$^3$, [4.27]</td>
<td>4.02x10$^3$, [4.27]</td>
</tr>
<tr>
<td>$\Sigma A_{ik}$ [s$^{-1}$]</td>
<td>3.69x10$^3$, [4.27]</td>
<td>4.47x10$^3$, [4.27]</td>
<td>4.02x10$^3$, [4.27]</td>
</tr>
<tr>
<td>$k_{e^{-}f(E/N)}$ [cm$^3$/s]</td>
<td>f(E/N), [4.28]</td>
<td>f(E/N), [4.29]</td>
<td>f(E/N), [4.29]</td>
</tr>
<tr>
<td>$k_{O-O_2}$ [cm$^3$/s]</td>
<td>1.08x10$^9$, [4.30]</td>
<td>7.6x10$^{10}$, [4.30]</td>
<td>7.6x10$^{10}$, est.</td>
</tr>
<tr>
<td>$k_{O-He}$ [cm$^3$/s]</td>
<td>1.0x10$^{-13}$, est.</td>
<td>4.5x10$^{-12}$, [4.31]</td>
<td>4.5x10$^{-12}$, [4.31]</td>
</tr>
</tbody>
</table>

A typical actinometry spectrum is shown in Fig. 4.12; various Ar(2p) emissions are visible along with the 777-nm emission of atomic oxygen and the ro-vibrational emission of
O₂(b). The Ar(2p) emission at 763 nm interferes with the spectra of O₂(b), and therefore it is necessary to take an additional scan in similar plasma conditions with the trace Ar flow turned off in order to obtain the temperature from the O₂(b) spectra for use in data reduction. Using fiber collection, it was possible to rapidly collect similar spectra along the length of the discharge tube to determine the buildup of atoms along the discharge length. For the Apogee CCD/PI-Acton spectrometer system described above, an integration time of three seconds was typical with argon flow rates of less than 5% of the oxygen flow.

![Sample spectrum showing oxygen and argon excited state emissions, along with the emission of O₂(b) at 761.9 nm.](image)

Figure 4.12. Sample spectrum showing oxygen and argon excited state emissions, along with the emission of O₂(b) at 761.9 nm.

### 4.4.3. Braginsky Secondary Discharge Actinometry Technique

TAA can also be applied in the discharge effluent (flow downstream of the discharge exit) using the method developed by Braginsky [4.31]. In this method, Ar actinometry is applied to a small, low power discharge ignited in the flow tube downstream of the primary discharge. A typical diagnostic setup where this technique was applied is sketched in Fig. 4.13 (taken from work in [4.21]). As will be discussed in Section 5, this method was in good agreement with titration results, and allows spatial measurement of atoms downstream of the discharge and is minimally invasive compared to NO₂ titration.
Figure 4.13. Schematic of ElectricOIL setup used for making measurements of oxygen atoms using both NO\textsubscript{2} titration and secondary discharge actinometry downstream of a hollow cathode RF discharge. The setup of the O\textsubscript{3} absorption diagnostic is also shown.

4.4.4. Determination of E/N using Argon or Atomic Oxygen Emissions

The calibration factor $K_{\text{Ar/O}}$ in Eqn. 4.14 can be determined either from comparison of actinometry to airglow results or by modeling the pumping rates of various excited states using cross-section data and the EEDF (as described in Section 2). Figure 4.14 shows the cross-section data for pumping of the O* and Ar* states (taken from Laher [4.28] and Ballou [4.29] respectively). The ratio of pumping rates can be determined as a function of $E/N$, and coupled with quenching and spontaneous emission rates for O(3p\textsuperscript{5}P) and Ar(2p\textsubscript{1}) to determine $K_{\text{Ar/O}}$ as a function of mixture, discharge $E/N$, and pressure. The results for this calculation using the above cross-section data, and EEDFs from the Boltzmann solver for a 10:33 mixture of O\textsubscript{2}:He are shown in Fig. 4.15. $K_{\text{Ar/O}}$ increases with pressure due to the effect of quenching, and is a strong function of $E/N$. The strong dependence on $E/N$ occurs because of the difference in threshold between Ar(2p\textsubscript{1}) (13.48 eV), and O(3p\textsuperscript{5}P) (10.74 eV). As $E/N$ increases, the EEDF re-distributes to higher electron energies, and the pumping of Ar(2p\textsubscript{1}) increases with respect to the pumping of O(3p\textsuperscript{5}P).
The calculation in Fig. 4.15 highlights an interesting problem which must be solved if TAA is to be applied in moderate pressure cases and without the use of an airglow method for calibration which was the approach used in early work (for example Figs. 4.10). In order to bypass the reliance on airglow measurements, a measurement technique for $E/N$ is necessary. A technique for $E/N$ measurement that is prevalent in the literature, and applied to a variety of discharge regimes is the use of trace rare gas emission spectroscopy (TRGES). In this technique, a trace amount of rare (noble) gas is introduced to the discharge, and the various emissions from the rare gas excited states are compared to a collisional-radiative model of the emissions as a function of $E/N$ (EEDF). A good example of a collisional-radiative model is in the work by Navartil et. al, where a detailed model of neon emissions was developed and used to analyze 1 Torr neon plasma in the $E/N$ range of 2-20 Td [4.31]. In such a model, the rate of production of various states by direct electron-impact is given by the product $k_{ij}n_e[M]$ where $n_e$ is the electron density, and

$$k_{ij} = \int_{\varepsilon_i}^{\infty} \sigma_{ij}(\varepsilon) \nu(\varepsilon) F(\varepsilon) d\varepsilon$$  \hspace{1cm} \text{(Eqn. 4.15)}$$

In Eqn. 4.15, $i$ denotes the initial state (M) and $j$ denotes the final state (M*) such that $k_{ij}$ is the rate coefficient for production of state $j$ from state $i$, $\sigma_{ij}$ is the energy-dependent cross-
section for the process excitation of \( j \) from \( i \), \( v \) is the electron velocity as a function of electron energy, and \( F(\epsilon) \) is the normalized electron energy distribution function \( (\int_{0}^{\infty} F(\epsilon) d\epsilon = 1) \). This rate equation is used to model the relative intensity of various emissions as a function of \( E/N \) (as in Eqn. 4.13 for actinometry). The spectroscopic measurements of the rare gas emissions from various states in the discharge are then compared to the modeling results in order to deduce the \( E/N \). This method is readily applied to emissions from Ar* emissions measured when argon is introduced to the discharge for actinometry.

A similar technique to TRGES was used by Pagnon et al. [4.24], where instead oxygen atom line ratios were used to deduce the \( E/N \). In particular the ratio of the O(3p\( ^5 \)P) 777-nm emission to the O(3p\( ^3 \)P) 844-nm emission was measured in an oxygen DC glow discharge and compared to E-field measured by a set of Langmuir probes and density determined from pressure measurements and the temperatures deduced from O\( _2 \)(b) spectra [4.24]. Pagnon et al. obtained agreement of 20% between these two methods [4.24]. This technique is easily applied to ElectricOIL work using similar modeling as applied in actinometry. Pumping rates of O(3p\( ^5 \)P) and O(3p\( ^3 \)P) are modeled as a function of E/N using Eqn. 4.15, and the intensities of each are modeled using Eqn. 4.13.

The basic goal of this technique is to draw a simple correlation between the discharge \( E/N \) and the ratio of emission lines. For example, Pagnon’s method was to use the relation

\[
\frac{I_{844}}{I_{777}} = \frac{h\nu_{844} A_{ij}^{3p} \sum k_A k_e \left(k_e^{3p} \right) \sum m \left[k_e^{3p} \right]}{h\nu_{777} A_{ij}^{3p} \sum k_A k_e \left(k_e^{3p} \right) \sum m \left[k_e^{3p} \right]} = f\left(\frac{E}{N}\right)
\]

(Eqn. 4.16)

The emission ratio is calculated as a function of \( E/N \), and measured ratio is compared to the calculated value to deduce the \( E/N \). This method, along with a similar method comparing Ar(2p) emissions ratios were investigated as a means to measure the \( E/N \) in RF discharges at moderate pressures. The results will be discussed in Section 7.

### 4.5. Optical Diagnostics Discussion

This section has described a variety of diagnostics which have been used to study O\( _2 \)/He discharges for use in ElectricOIL. In the following sections, data from the diagnostics discussed here will be used to describe the performance characteristics of various discharge configurations which have been investigated for use in ElectricOIL technology.
References


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5. Lessons Learned in Early ElectricOIL Studies

The goal of this section is to review a variety of key lessons learned in early ElectricOIL development though various experimental investigations. These lessons involve (i) developmental approach using small scale systems, (ii) early kinetics investigations discovering the role of oxygen atoms, and the use of NO\textsubscript{X} to control oxygen atoms and enhance O\textsubscript{2}(a) production, (iii) the application of trace argon actinometry as a minimally invasive technique to measure O-atom production, and (iv) the dependence of O\textsubscript{2}(a) with specific energy deposition (power per O\textsubscript{2} flow rate), and the influence of discharge parameters (configuration, frequency, etc.) on O\textsubscript{2}(a) production efficiency.

5.1. Developmental Approach

At this time there are a significant number of large, high-power gas lasers systems (see for example reference [5.1]), so it seems that it would be trivial to begin design of a large-scale EOIL device. There are large-scale COIL devices, and there are large-scale CO\textsubscript{2} lasers which operate using a discharge as the gain medium. So, the fastest approach might seem to be to build a device that operates at similar flow rate to existing high-power COILs, and simply replaces the chemical singlet-oxygen generator (SOG) with a large volume oxygen discharge. However, with EOIL this is not the case, and the most significant progress was attained using small-scale systems operating at relatively low pressures and flow rates [5.2, 5.3, 5.4]. The relatively small scale of these devices offered the possibility of detailed investigations of system dynamics. This is historically the same approach that was taken in the development of COIL beginning in 1960 and continuing into the 1990s [5.5]. Fundamental science suggested the possibility of a COIL, laser was achieved in a small system [5.6], and then systematic improvements were made [5.5]. This began with basic scaling of the subsonic system, which included kinetics studies (O\textsubscript{2}(a) pooling, I\textsubscript{2} mixing/dissociation) and advancements in O\textsubscript{2}(a) generator technology. This was in turn followed by demonstration of supersonic COIL which increased efficiency, improved beam quality, and decreased the size of the device [5.5]. This was followed by further refinements: high pressure operation, O\textsubscript{2}(a) transport efficiency, H\textsubscript{2}O (quencher) removal [5.5]. Once efficiency was improved, scaling to high powers proceeded [5.5]. As described in Section 2, the make-up of an electric oxygen-iodine laser introduces a new scenario of
kinetics which must be explored in order to understand the system fully. Thus, the new electric oxygen-iodine laser technology must be allowed to “mature” as did COIL. One phase of this developmental process was careful study of the discharge production of excited states, and the system kinetics using the various diagnostic techniques available.

5.2. Early Important Kinetics Observations

The number of diagnostics that were introduced to study the ElectricOIL system allowed a pathway to achieving positive gain and eventually lasing, and the ability to study the system in order to improve performance [5.7]. Some important early observations were:

1. Oxygen atoms rapidly quench the laser state I*, removing the energy transported by O2(a) through the forward/reverse pumping reaction (O2(a) + I ⇌ O2 + I*).
2. Oxygen atoms can be removed by NOX to eliminate quenching.
3. Diluents can be used in a beneficial role to obtain higher O2(a) efficiency, and lower flow temperature.
4. Introduction of NOX to the discharge improves O2(a) production.

5.2.1. Removing Oxygen Atoms to Maintain O2(a)

Perhaps the most important experiment to ElectricOIL technology was the one in which it was realized that oxygen atoms were quenching the laser state I*. The data was reported thoroughly by Carroll et al. [5.7] and by Woodard [5.8], while here it is reported in a condensed version. A 25.4 cm gap LCCRF hollow-cathode discharge in a 49 mm I.D. tube had been well developed for low pressure operation (few to 20 Torr), and generated substantial O2(a) yield (14-18%) [5.8]. However, when iodine was injected downstream of the discharge, the O2(a) decayed rapidly downstream of the injector as evidenced by a substantial decrease in emission at 1268 nm with distance. The oxygen atom flow rate was determined to be linear with power using NO2 titration. The O2(a) measured at the diagnostic block without I2 in the flow is maximized at 500 W input. When I2 is introduced, the level of O2(a) drops significantly, with the maximum signal at ~200 W input. The O2(a) and oxygen atom titration data from this experiment is shown in Fig. 5.1. As shown in Fig. 5.2, when NO2 is introduced between the discharge and I2 injector (I2 flow rate ~6 µmol/s), the level of O2(a) at the diagnostic port downstream of the I2 injector was improved, and at 1 mmol/s
NO₂ (25% of the total oxygen flow rate), the O₂(a) density was measured to be nearly the same as without I₂.

Figure 5.1. 1268 nm emission of O₂(a) and oxygen atom flow rate as a function of RF power with and without I₂ injection. The flow conditions are 4:16 mmol/s O₂:He at 10 Torr. The discharge is a LCCRF version with hollow cathodes separated by 25.4 cm in a 4.9 cm I.D. tube.

Figure 5.2. 1268 nm emission of O₂(a) and 1315 nm emission of I* as a function of RF power with varied NO₂ flow (mmol/s) injected between the discharge and I₂ injector. The discharge flow conditions and configuration are as in Fig. 5.1.

The data in Figs. 5.1 and 5.2 was used to conclude that oxygen atoms were quenching I* by the process I* + O → I + O. As discussed in Section 2, this reaction was found to have a rapid rate of 8x10⁻¹² cm³/s, only a factor of 3.4 less than the backward rate of the pumping reaction at room temperature (2.7x10⁻¹¹ cm³/s). Therefore, the rapid quenching of I* by O removes energy stored in O₂(a) by interrupting the reverse process of the near-resonant energy transfer between O₂(a) and I*. However, this problem was solved by removing the oxygen atoms via NO₂ titration upstream of the I₂ injection leading to positive gain in the supersonic cavity region. In the first report of laser output from ElectricOIL, better gain conditions were achieved when NO was introduced through the discharge, which also reduced oxygen atom flow rate through similar kinetics [5.2]. The kinetics and mixing of I₂ downstream of the discharge where modeled extensively by Palla et al. [5.9], resulting in excellent agreement with the experimental measurements of excited states and gain [5.7] through updates to the kinetics and improvements to the mixing model.
5.2.2 The Effect of Diluents

A lot of early experimental and modeling work in ElectricOIL focused on determining the best mixture of oxygen and diluents to provide the best O₂(a) production and temperature performance. The modeling work indicated that helium or argon diluent could be used to shift the discharge $E/N$ to lower values where O₂(a) production would be optimized [5.10]. Carroll et al. investigated O₂(a) production in a 25.4 cm gap, 4.9 cm I.D. longitudinal capacitively-coupled RF (LCCRF) discharge with 2 Torr partial pressure of O₂, and power inputs in the range of 50-400 W [5.11]. Three cases were investigated: (i) pure O₂, (ii) 1:3 O₂:Ar and (iii) 1:4 O₂:He. With pure O₂, the $E/N$ was in the range 20-30 Td, while the introduction of diluents (cases ii and iii) resulted in the range 5-10 Td ($1 \text{Td} = 1 \times 10^{-17} \text{ V-cm}^2$). The O₂(a) production was similar for the pure O₂ case (i) and the 1:3 O₂:Ar case (ii), but in the 1:4 O₂:He case, the peak O₂(a) counts at 1268 nm were improved by better than a factor of 2 (15 to 38 mV). The introduction of diluents also significantly reduced the flow temperature which was approximately linear with power; for pure O₂ the slope was ~1.1 K/W, for 1:3 O₂:Ar it was ~0.57 K/W, and for 1:4 O₂:He it was 0.37 K/W. This experiment established that the use of He diluent led to substantial discharge performance improvements favorable for ElectricOIL: (1) lowering the $E/N$ which led to improved O₂(a) yield and power stored in O₂(a) (by ~63% accounting for temperature), and (2) significantly less temperature rise with power deposition. The modeling of this experiment in GlobalKin (see [5.10]) resulted in some discrepancies. While the temperature performance was well replicated, the calculation of yield did not agree with experiment, due to kinetics lacking from the model; this is not surprising considering that the introduction of diluents significantly increases the residence time in the discharge and post-discharge region which would amplify these effects. It was anticipated based on modeling results that the performance would be better with Ar due to lower inelastic losses compared to He ($p_{elastic} \sim m_e/M$, see Section 2), however experimental investigations demonstrated that the yield with Ar diluent decreased significantly [5.11]. The influence of helium diluent is well illustrated by the data from an inductive discharge shown in Figs. 5.3 (O₂(a) yield) and 5.4 ([O₂(a)]). O₂(a) was measured 55 cm downstream of the discharge coil. As helium diluent is added (for constant O₂ flow rate of 5 mmol/s, and constant pressure), the discharge temperature (at highest power) decreases significantly from 515 K at 5:0 O₂:He to 375 K at 5:50 O₂:He, while the O₂(a)
yield improves significantly. For 5 mmol/s O₂ input, the best O₂(a) yield occurs at high
diluent ratio (5:50 O₂:He), but the highest O₂(a) density occurs at 5:10 O₂:He. Lower O₂
flow rate (higher specific power, watts per millimole/s O₂) results in higher yield for the
same diluent ratio, as illustrated by the case with 3:16 mmol/s O₂:He.

![Figure 5.3. O₂(a) yield versus power measured (55 cm) downstream of an inductive discharge as a function of mmol/s O₂:He. The discharge pressure was 12.5 Torr. Pp is RFsys minus the power loss in the inductive coil.](image)

![Figure 5.4. O₂(a) density versus power measured (55 cm) downstream of an inductive discharge as a function of mmol/s O₂:He. The discharge pressure was 12.5 Torr.](image)

More recent experiments with transverse discharges have demonstrated significant fraction of
power into O₂(a) ~30% using O₂/He/Ar/NO mixtures [5.12]. Using high diluent ratios of
helium (20:1 O₂:He and trace NO) has allowed O₂(a) yields of ~25% using transverse
discharge [5.13]. A key result that must be realized from these studies [5.12, 5.13] is that
there is typically a tradeoff between O₂(a) yield and O₂(a) production efficiency; the overall
performance of the laser system depends on both of these. In addition, the gas mixture will
affect the EOIL nozzle performance. While a He/O₂ ratio of 6/1 usually gives the best yield
performance [5.13], lower ratios are typically required to give best overall ElectricOIL
performance (typically He/O₂ = 33/10 in recent work).
5.2.3. Improving $O_2(a)$ Production with NO

As discussed in Section 2, the production of $O_2(a)$ is controlled by the characteristic $E/N$ (electric field-to-gas density ratio) which along with the state of the gas species in the plasma determines the EEDF (electron energy distribution function). With this in mind, it was suggested that the introduction of various “sensitizers” (or gas impurities) to the discharge gas mixture could lead to control and optimization of the $O_2(a)$ production. There are many successful examples of this type of approach in discharge design. For example, Coburn and Chen optimized F atom production in etching discharges by varying mixture in CF$_4$/O$_2$ discharges to control the $E/N$ [5.14]. Another example is the work of Vagin et al. in which CO was introduced to stabilize an E-beam plasma in O$_2$ discharge through attachment ($e + CO \rightarrow CO^-$) [5.15]. Some sensitizers that were investigated in ElectricOIL discharge work were NO, NO$_2$, CO, N$_2$, and Xe. These tests used the 25.4 cm gap, 4.9 cm diameter LCCRF hollow cathode discharge. The goal of the experiments was to observe the impact of the sensitizers on $O_2(a)$ performance and discharge terminal characteristics (electrode voltage and current).

The work with CO was very inconclusive, and led to the coating of the downstream electrode with carbon, and arcing. Some results with Xe and N$_2$ showed little change in $O_2(a)$ density as the sensitizer flow rate increased. Tests with NO resulted in substantial benefit.

The introduction of NO to the mixture in the active discharge was considered as a way to lower the ionization potential (IP) of the gas (IP(NO) = 9.26 eV compared to IP(O$_2$) = 12.07 eV, and IP(He) = 24.59 eV), leading to a discharge sustained at lower $E/N$ [5.7]. It was demonstrated in experiment that the introduction of NO did in fact lower the voltage across the electrodes and a substantial increase in the $O_2(a)$ yield downstream of the discharge was also observed [5.7]. Some of the initial data is shown in Fig. 5.5. The $O_2(a)$ production improves significantly with added NO, but for the NO/O$_2$ ratio required to maximize the effect (~5%), the drop in the discharge voltage is only a few percent. The mechanism for improved $O_2(a)$ production with NO addition is convoluted because NO affects both the electrodynamics (lowered IP), and the gas-phase kinetics (removal of O-atoms). In addition, the introduction of NO to the discharge results in intense NIR emissions from NO excited states which make measurement of the 1268-nm emission from $O_2(a)$ difficult to measure.
within the discharge, and 1268-nm measurements are restricted to the flow tube downstream of the discharge.

![Figure 5.5. Discharge voltage and O$_2$(a) counts as a function of the ratio between the input NO and O$_2$. The baseline flow conditions are 5:20 mmol/s O$_2$:He at 10 Torr. The discharge configuration is a LCCRF version with hollow cathodes separated by 25.4 cm in a 4.9 cm I.D. tube. The amount of NO required to maximize the increase in O$_2$(a) is small, and has an insignificant impact on the voltage.]

5.3. Oxygen Atom Measurements

Oxygen atoms are produced in large percentages, comparable to O$_2$(a) at the discharge exit. Measuring oxygen atoms in ElectricOIL discharges is complicated by various issues associated with the plasma and afterglow regimes. For airglow methods, these issues are associated with the timescales of the kinetics relative to the residence time of the gases through the flow system, in particular the influence of three-body recombination mechanisms on the oxygen atom decay. With the actinometry methods, the problems are associated with quenching of excited states by the background gases (primarily He and O$_2$) and determination of the $E/N$ which determines the excited state pumping. With these issues accounted for, the airglow methods and the actinometry methods were found to be in good agreement, for several cases in which they were compared. With confidence drawn from initial comparisons to NO$_2$ titration and calibrated airglow techniques, the actinometry technique was used to determine oxygen atom flow rates in transverse discharge configurations which were designed to operate at higher flow rates and pressures.
5.3.1. NO2 Titration Data with High Flow Rate and Pressure

Early investigations of oxygen atoms in ElectricOIL used the Kaufman titration technique [5.16] (see Section 4.3.2). The procedure was to inject NO2 downstream of the discharge and measure the response of the PMT at 580 nm downstream of the NO2 injection as the NO2 flow rate varied. Following the observations of Kaufman, as NO2 flow rate increases the 580-nm emission initially increases, passes though a peak and then is extinguished; the flow rate at which the emission is extinguished corresponds to the initial oxygen atom flow rate, while the peak corresponds to half the oxygen atom flow rate. In other words, the PMT response is a parabola as a function of NO2 flow rate, corresponding to the product of \([O]\) decreasing linearly with NO2 flow rate, and \([NO]\) increasing linearly with NO2 flow rate. (i.e. the PMT response is a parabola with a peak at the NO2 flow rate corresponding to half the oxygen atoms flow rate). Therefore, in early experiments the oxygen atom flow rate was determined as twice the NO2 flow rate at the peak emission [5.17].

However, for high flow rates and pressures, the expected parabolic behavior of the O-NO airglow with NO2 flow rate becomes distorted due to the influence of 3-body recombination. In particular, the peak in the PMT response to NO2 moves to a flow rate lower than half the initial oxygen atom flow rate, and at some flow rate beyond the peak, the glow is extinguished. Some data showing this effect was shown in [5.17], but the kinetics were not addressed. As discussed in Section 4.3.2, the PMT response is well modeled analytically, when including the effects of three-body recombination (O+ NO + M \(\rightarrow\) NO2 + M). The studies by Rakhimova et al. concluded that the actual extinguishing point is in good agreement with the initial oxygen atom flow rate [5.18]. This analysis established that determining the O-atom flow rate as double the NO2 flow rate for peak PMT signal could produce results which were low by a factor of two or more for typical ElectricOIL flow conditions. In future use of NO2 titration, the NO2 flow rate at the actual extinguishing point, not the NO2 flow rate at the peak signal, was used to evaluate the oxygen atom flow rate.

Since oxygen atoms were found to be responsible for a significant amount of quenching in ElectricOIL, measures were taken to suppress them. With NO introduced to the discharge flow mixture (originally to decrease \(E/N\)), oxygen atoms formed in the discharge are decayed by three-body recombination and by the fast reaction \(O + NO2 \rightarrow O2 + NO\) with
NO₂ supplied by the three-body recombination. To determine the influence of NO on the oxygen atom flow rate, the NO₂ titration technique was applied to a typical operational laser flow rate condition (with NO in the discharge mixture), and to the same conditions without NO in the discharge flow [5.17]. The resulting data is shown in Fig. 5.6, and compared to a simple 1-dimensional, constant-temperature model of titration accounting only for the reactions (based on [5.18], see Section 4.3 for rates)

\[
O + NO₂ \rightarrow O₂ + NO, \quad \text{and} \\
O + NO + M \rightarrow NO₂ + M, \quad M = O₂, O, He
\]

For the data set without NO through the primary discharge, the NO₂ flow rate at the extinguishing point which corresponds to the oxygen flow rate from the discharge is a factor of 6 higher than the NO₂ flow rate corresponding to the peak signal, not a factor of 2 as expected for Kaufman NO₂ titration at low flow rates and pressures [5.16].

Figure 5.6. NO₂* 580-nm signal as a function of NO₂ flow rate with and without NO in the discharge flow compared to analytical model of NO₂ titration. The discharge flow is 3:16 O₂:He at 12.5 Torr, with 500 W RF. The discharge used was a 25.4 cm gap, 4.9 cm diameter LCCRF hollow cathode discharge. The case without NO is consistent with 0.54 mmol/s of oxygen atoms. When 0.15 mmol/s is added to the discharge flow, the response of PMT is strictly decreasing with added NO₂, and the airglow is extinguished in the neighborhood of 0.2 mmol/s NO₂. The model assumes 425 K in both cases which is similar to the O₂(b) temperatures measured in the experiment. Work by Rakhimova et al. [5.18] in Fluent and using an analytical model determined the oxygen atom flow rate which matched the response in the no NO case to be 0.54 mmol/s.
The data and modeling in Fig. 5.6 establishes that the NO₂ titration technique can be used to determine oxygen atom flow rates with and without NO in the discharge mixture, and that the NO₂ flow rate at the extinguishing point of the airglow corresponds well to the initial flow rate of oxygen atoms. While the location of the peak intensity and the extinguishing point are well replicated by the model, the shapes of the curves are dissimilar. This is likely due to the influences of mixing and non-uniform distributions of temperature and velocity through the tube cross-section at the PMT location.

5.3.2. Comparison of Ar Actinometry and NO₂ titration

Use of the NO₂ titration technique with typical ElectricOIL flow regime can be quite complicated, due to the detailed analysis required to account for recombination and mixing effects. In addition, the method is invasive as it requires flow rates similar to the total oxygen flow rate to be introduced, and it can not be used in the discharge because the introduction of NO₂ disturbs the discharge electrodynamics, and the PMT can be influenced by other discharge emissions besides that from O-NO recombination. Therefore, trace argon actinometry techniques, as described in Section 4.4 were investigated. Initially, these were applied using the secondary discharge technique as introduced by Braginsky et al. [5.19], compared directly to NO₂ titration in the discharge afterglow region.

Figure 5.7 compares the oxygen atom flow rates determined from the NO₂ titration technique and the calibrated argon actinometry technique. The flow rate determined from the actinometry is the ratio of the O*(777-nm) and Ar*(750.4-nm) lines times the input ratio of Ar to O₂ multiplied by a calibration constant, with the small baseline signal due to the 20-W secondary subtracted. The calibration constant was found by minimizing the square-root sum of the squares of the difference between the calibrated actinometry data and the linear fit to the NO₂ titration data. The agreement of the two data sets was encouraging. However, the influence of each discharge on the other must be considered and minimized. The 20-W secondary discharge produces a small amount of dissociation by itself, corresponding to ~0.065 mmol/s on the calibrated scale (removed in Fig. 5.7). Also, the primary discharge pumps the O* in the secondary discharge region through UV excitation. Figure 5.8 shows the O*(777-nm) signal with and without the secondary discharge. The O* signal in the
secondary region with only the primary discharge excitation is at most 3% of the signal with the secondary engaged and can easily be compensated for during calibration.

![Figure 5.7](image1.png)

Figure 5.7. A comparison of the Ar actinometry and NO\(_2\) titration techniques for determining O- atoms. The mixture was 3:16:0.05 O\(_2\):He:Ar at 6.5 Torr. The secondary discharge was 20 W capacitive RF. The calibration constant \(C = 1.04\).

![Figure 5.8](image2.png)

Figure 5.8. The influence of the primary discharge on O*(777-nm) signal in the secondary discharge region. The mixture was 3:16:0.05 O\(_2\):He:Ar at 6.5 Torr. The secondary discharge was a 20 W capacitive RF.

5.3.3. \textit{Ar Actinometry with NO in the Primary Discharge}

In another experiment, the effect of NO on the actinometry technique was investigated, measuring the O*(777-nm) and Ar*(750.4-nm) emissions within the primary LCCRF discharge [5.17]. The O*/Ar* ratio was measured as a function of power for a discharge flow of 3:16:0.05 O\(_2\):He:Ar at 12.5 Torr. This result, shown in Fig. 5.9 was encouraging, considering that the actinometry technique measures a linear response of atoms with power in the presence of NO, however, the effects of NO on the discharge pumping of argon and oxygen states illustrates a higher level of complexity. In the data given in Fig. 5.9, the addition of NO resulted in a reduction of Ar(2p) emissions, which indicates that the pumping mechanisms are affected. A collision between argon metastables and NO most likely results in the ionization of NO, removing the former from the excitation routes for both Ar* and O*. In future applications, it was assumed that trace NO has little impact on the pumping dynamics, although it might change ratios of Ar(2p) emissions by altering the discharge \(E/N\).
5.4. Early Work with RF Discharge Configurations

Some important observations made with RF discharges were

1. O$_2$(a) tends to “scale” with power per molar flow rate
2. ICRF and LCCRF offered similar O$_2$(a) performance at low pressures
3. TCCRF discharges offered better high pressure operation
4. Excitation frequency influences O$_2$(a) production in capacitive discharges

5.4.1. O$_2$(a) Yield versus Energy Deposition

There is a tendency for the O$_2$(a) yield from the RF discharge to “scale” with energy deposition, typically defined as either the ratio of input power to input molar flow rate of oxygen W/(mmol/s, O$_2$), or the proportional parameter, energy (in eV) deposited per input molecule of oxygen eV/(molecule O$_2$) (for reference, 1 eV/molec(O$_2$) = 96.4 W/(mmol/s, O$_2$). Early modeling work specified that the later parameter should be in the range 5-8 eV/molecule (482 – 771 J/mmol) to maximize the O$_2$(a) yield [5.20, 5.21]. The results plotted in Figures 5.10.a-c were obtained using a 25.4 cm gap, 4.9 cm diameter LCCRF hollow cathode discharge operating in the range of 0-600 W with a O$_2$:He ratio of 10:33, and a constant 0.15 mmol/s NO. Figure 5.10.a shows data for constant O$_2$ (and He) flow rate with varied pressure; there is some decrease in yield slope with energy deposition as pressure increases, likely due to increased quenching, as was the case with the modeling result [5.20].

Figure 5.9. Oxygen atom flow rate determined from argon actinometry ratio in the primary longitudinal discharge without and with NO. The discharge flow is 3:16:0.05 He:O$_2$:Ar at 12.5 Torr. The calibration factor was determined by comparing NO$_2$ titration to Ar actinometry in secondary discharge.
Figure 5.10.b shows similar data where pressure is held constant while the molar flow rate of O$_2$ varies between 3.6 and 10 mmol/s. For constant pressure, there is significantly less scatter, and for this discharge configuration the yield becomes non-linear with energy deposition at ~50 J/mmol, and reaches a maximum (near 14% for the lowest flow rate case) between 100 and 150 J/mmol. This maximum yield value is roughly half of the best modeling predictions (~30%), and occurs at a significantly lower energy deposition. Figure 5.10.c shows the O$_2$(a) production efficiency for the cases in Fig. 5.10.a and b; The efficiency is fairly flat in the 0-50 J/mmol range, decreasing with pressure; above 50 J/mmol, the efficiency decreases linearly.

Figure 5.10. O$_2$(a) yield and production efficiency as a function of O$_2$ specific energy deposition in a 25.4 cm gap, 4.9 cm diameter LCCRF hollow cathode discharge operating in the range of 0-600 W with a O$_2$:He ratio of 10:33, and a constant 0.15 mmol/s NO; (a) constant oxygen flow rate with varied pressure (b) constant pressure with varied oxygen flow rate, and (c) O$_2$(a) production efficiency for cases in both (a) and (b). The measurements were made 59 cm downstream of the hollow cathode gap. $f = 13.56$ MHz.
5.4.2. Discharge Configurations Studies

A number of discharge configurations have been investigated for use in electric oxygen-iodine lasers. Successful demonstrations have been made with RF types [5.2], microwave configurations [5.3], and pulsed / DC sustainer configurations [5.4]. The UIUC/CU Aerospace group has studied all three of these discharge categories; see for examples [5.20] (microwave work) and [5.22] (pulsed-sustainer work). Of the investigated specifically for the UIUC/CU Aerospace ElectricOIL, the RF configurations have been most successful. The discharge used in the first successful ElectricOIL demonstration was a longitudinal capacitive coupled RF (LCCRF) discharge in a 4.9 ID tube [5.3], but it was found early on that an inductively-coupled RF (ICRF) discharge ignited in the same size tube could produce very similar O_2(a) yield and efficiency [5.7], for example ~18% O_2(a) for 400 W deposited into a 3:16:0.15 mmol/s mixture of O_2:He:NO. However, both of these discharge configurations had stability issues at high power inputs and pressures which typically resulted in poor O_2(a) production. This prompted the study of transverse capacitive coupled RF (TCCRF) discharge, which offered improved performance at higher operating pressures. A comparison of O_2(a) production in LCCRF hollow cathode (HC) and TCCRF “clamshell” (CS) discharges is shown in Fig. 5.11. The TCCRF discharge produced better O_2(a) yield than LCCRF at 16 Torr, and produced similar yield at 24 Torr. While the O_2(a) yield performance improved, the magnitude and general trend in O_2(a) production efficiency is similar, as shown in Fig. 5.12 (compare to HC results in Fig. 5.10).
5.4.3. Frequency Influence in RF discharges

A parameter that influences RF discharge behavior is the excitation frequency ($\omega = 2\pi f$). In general, this is because the motion of electrons, the major charge carriers, is dictated by the relative magnitudes of the excitation (oscillation) $\omega$, plasma $\omega_p$, and collision frequencies $\nu_m$ [5.23]. The excitation frequency is dictated by the source, the plasma frequency is dictated by the degree of ionization (electron density), and the collision frequency is dictated by the gas mixture and density and electron thermal velocity. The typical regime which has been studied in ElectricOIL work has been characterized by $\omega \ll \omega_p$, $\omega_p \sim \nu_m$. Rakhimova et al. suggested that increased excitation frequency should reduce the RF plasma sheath thickness, allowing more volume for the bulk plasma in which O$_2$(a) is excited [5.24]. The sheath thickness should scale with the displacement amplitude $A_{osc}$ of electron drift oscillations in the field amplitude $E$, which is given by $A_{osc} = eE / m \nu_m \omega$ (derived assuming $\nu_m \gg \omega$) [5.23].

In ElectricOIL work by the UIUC/CUA group, the influence of frequency was studied initially with LCCRF hollow cathode discharge where the effect were found to be
mildly useful in enhancing O$_2$(a) production. Figure 5.13 shows O$_2$(a) density measurements in a 25.4-cm gap LCCRF hollow cathode discharge for varied frequency with and without NO. For the cases without NO, [O$_2$(a)] is improved at higher powers as frequency increases; for the cases with NO added to the discharge mixture, the influence of frequency on [O$_2$(a)] is less significant, showing a slight improvement for the 28.3 MHz case compared to the lower frequencies. As shown in Fig. 5.14, the oxygen atoms produced by the hollow cathode configuration at these conditions did not vary significantly with excitation frequency.

The influence of excitation frequency in TCCRF discharges was also studied, where the effects were found to be much more crucial. Figure 5.15 compares the O$_2$(a) yield measured downstream of the transverse “clamshell” discharge (4.9 cm ID x 25.4 cm electrode length) as a function of power at 13.9 and 29.3 MHz without and with NO. Both without and with NO, the O$_2$(a) yield is improved by operating the discharge at increased frequency. As shown in Fig. 5.16, the levels of O$_2$(b) measured at the downstream location are also affected, showing a significant change in behavior due to NO. Without NO, the level of O$_2$(b) downstream decreases with power, due to rapid quenching by O-atoms. The addition
of NO reduces the O-atom flow rate, and higher level of \( \text{O}_2(\text{b}) \) are observed at the downstream measurement location at high power. Increasing the excitation frequency results in an increase in \( \text{O}_2(\text{b}) \) levels at higher power inputs, but in general the \( \text{O}_2(\text{b}) \) yield is small (< 0.1 % at this location).

Figure 5.15. \( \text{O}_2(\text{a}) \) yield versus RF power for varied excitation frequency in the 4.9 cm ID x 25.4 cm transverse “clamshell” discharge without and with NO in the flow mixture. The flow conditions are 3:16 \( \text{O}_2: \text{He} \) at 12.5 Torr. The added NO flow rate is 0.15 mmol/s. The measurement is made 54 cm downstream of the discharge exit.

Figure 5.16. \( \text{O}_2(\text{b}) \) yield versus RF power for the same cases shown in Fig. 5.15.

5.5. Summary of Lessons Learned from Early Work

From the early diagnostic work with ElectricOIL, some key “lessons” were learned and should be summarized. These lessons are:

1) **Small Scale Systems:** Use of small scale devices to study dynamics allows quick insight into the factors which drive those dynamics, and allows an important test bed for both discovering and exploring engineering solutions to laser system performance problems.

2) **Role of Oxygen Atoms:** The oxygen atoms produced in the discharge play a dual role in system kinetics. The O-atoms act as a quencher of the precursor \( \text{O}_2(\text{a}) \), and of the laser state \( \text{I}^* \). Also, they introduce a rapid \( \text{I}_2 \) dissociation mechanism which dominates the mechanisms typically found in COIL. The importance of these roles was realized through careful measurements of O-atoms, \( \text{O}_2(\text{a}) \), and \( \text{I}^* \) in the \( \text{I}_2 \) mixing region [5.7], and modeling
of the post-discharge kinetics using BLAZE [5.9] has resulted in good agreement with the observed behaviors.

3) Removing/Suppressing Oxygen Atoms: The first EOIL was made possible by removal of the O-atoms using NO₂ titration (to establish positive gain at first), and later, NO was passed through the discharge with the primary flow, which improved O₂(a) production in the discharge, suppressed O-atom production, and increased the recombination rate of O-atoms downstream. In later work with ozone absorption measurements, it was found that using NO to suppress and remove O-atoms from the system also significantly reduces buildup of ozone, which is a rapid O₂(a) quencher.

4) Measurements of Oxygen Atoms: Because oxygen atoms affect the EOIL system dynamics within the discharge and in the mixing and laser cavity regions, it was important to develop diagnostics for measuring O-atom levels throughout the system. Initial work made use of NO₂ titration, which was limited to measurements at a fixed location downstream of the discharge. Early measurements with trace Ar actinometry (TAA) in a secondary discharge showed good agreement with NO₂ titration measurements. Applying NO₂ titration in high flow rate, high pressure conditions, and with NO in the flow proved difficult, requiring substantial modeling of flow conditions to obtain meaningful results. Ar actinometry coupled with calibrated airglow measurements (Piper method) offered a convenient method for addressing this issue.

5) Dependence of O₂(a) on Power per O₂ Flowrate, W₀₂: As power is increased in an RF discharge in oxygen, the O₂(a) yield first increases (linearly) with power, then reaches a maximum, and then decreases with power. This process is due primarily to the effect of super-elastic collisions (O₂(a) returning power to the electron gas as [O₂(a)]/[O₂] increases), and secondarily to the buildup of quenchers, and removal of ground state by dissociation. Studies with LCCRF discharge configurations showed that the initial slope as a function of power and saturation observed at high power both scale with power per molar flow rate of O₂, or O₂ specific power deposition, W₀₂.

6) Discharge Selection: In early work, many discharge techniques were applied to work with EOILs, and many were found to produce sufficient O₂(a) for use in an EOIL. The EOIL has been demonstrated using RF, pulsed-sustainer, and microwave discharge configurations. RF discharges were easily applied, either in inductive or capacitive coupling
configurations. In work by the group at UIUC/CUA, work with pulsed-sustainer configurations showed some promise, but RF configurations using commercially-available equipment and simple matching network designs proved to be a much more reliable and robust approach. With use of transverse RF discharges, some interesting routes to improving system efficiency were discovered; early work showed that O₂(a) production could be improved by proper selection of various discharge parameters such as geometry or excitation frequency.

References


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6. Transverse Capacitive Radio-Frequency Discharge Studies

Experimental investigations of transverse capacitively-coupled radio-frequency (TCCRF) discharges in O₂/He/NO mixtures have indicated that O₂(α) production is a strong function of geometry, excitation frequency, pressure, and diluent ratio [6.1, 6.2]. The goal of these investigations was to maximize both the yield and flow rate (power flux) of O₂(α) in order to produce favorable conditions for application to an electric oxygen-iodine laser (ElectricOIL). In this section, behaviors of typical ElectricOIL TCCRF discharges in O₂/He/NO mixtures are discussed, showing the influence of various parameters on O₂(α) and oxygen atom production in the discharge pressure range of 1-100 Torr, with typical oxygen input flow rate of 10 mmol/s and power input range of 0.1 to 1.2 kW. Using varied discharge geometries, excitation frequencies, and optimizing He/O₂ diluent ratio it was possible to obtain O₂(α) yields of ~13% at 50 Torr, and ~16% at 20 Torr, corresponding to power carried by O₂(α) of 120 W and 150 W respectively. Over the range of 5-50 Torr, O₂(α) production efficiencies in the range 15-22% were possible.

6.1. Background on Transverse Capacitive RF Discharges

A prominent discharge technique used to produce O₂(α) in EOIL research has been transverse capacitive RF [6.1-6.8]. Experiments and modeling by Rakhimova et al. [6.3, 6.4] and Braginsky et al. [6.5-6.7] have shown that O₂(α) generation in transverse RF discharges can be significantly enhanced by exciting the discharge at higher frequencies than the typical 13.56 MHz. Rakhimova et al. [6.3] suggested that increased frequency led to a narrowing of the sheath region in which O₂(α) production is ineffective and allowed operation of the discharge in the homogeneous α-mode to higher energy inputs. Braginsky et al. [6.5] showed that increasing the excitation frequency in a small-diameter transverse discharge (from the typical 13.56 MHz) results in a substantial increase in O₂(α) production efficiency; with the addition of NO to the mixture and HgO-coated walls to enhance oxygen atom recombination, this group [6.5] obtained O₂(α) yields of ~21% at 10 Torr, ~17% at 20 Torr, and ~13% at 30 Torr using an excitation frequency of 160 MHz [6.5]. For these results, the input velocity and temperature were 10 m-s⁻¹ and 293 K respectively, and the tube internal diameter was 7 mm [6.5], which corresponds to increasing input oxygen flow rates in the
range 0.2-0.6 mmol/s over the 10-30 Torr pressure range. Using these values for yield and flow rate, the power carried by O$_2$(a) $P_{O_2(a)}$ was in the range of 4-8 W.

In various works by Braginsky et al. [6.6, 6.7] with capacitive RF discharges, three operating regimes (I$\to$III) were identified for increasing energy deposition into the plasma:

I) Homogeneous mode ($\alpha$-mode): energy is deposited approximately uniformly across the tube volume between the electrodes, and the discharge is sustained by volume ionization.

II) Transition mode ($\gamma$-mode): $\gamma$-processes (secondary electron emission) become essential for retaining the discharge structure, but the main energy is still dissipated in the interelectrode gap.

III) Inhomogeneous mode: plasma jets and surface wave discharge propagate outside the electrode gap and a large portion of the energy dissipation occurs outside of the gap. A considerable contribution of $\gamma$-processes to the electron generation is indicated by bright narrow near-electrode layers and a dark Faraday space within the interelectrode gap.

The homogeneous $\alpha$-mode is more favorable because it results in more efficient energy deposition into O$_2$(a) [6.7]. However, the maximum O$_2$(a) production (yield) often occurs at energy depositions at which the discharge is in $\gamma$-mode [6.7]. This description of operational modes for flowing RF discharges is consistent with the designations for $\alpha$ and $\gamma$ mode found in RF systems first noted by Levitskii [6.9]. Raizer et al. [6.10] provide numerous examples of capacitive RF discharge behavior in a variety of gas mixtures at moderate pressures (10-100 Torr), the regime of interest in EOIL.

An important characteristic of $\alpha$-mode RF transverse capacitive discharges is the “normal current density.” In the condition where energy deposition is low and the discharge does not fill the electrode gap (normal mode), as the current is raised, the discharge volume grows such that the current density remains nearly constant; this constant density is the “normal current density”, denoted $J_{\alpha}$ (see Raizer [6.10]), and corresponds to a minimum in the current-voltage characteristic (CVC) of the homogeneous $\alpha$-mode discharge. From work by Yatsenko [6.11] with He and Air discharges, the following trends can be expected: (1) $J_{\alpha}$ varies with mixture, (2) $J_{\alpha}$ increases with pressure, (3) $J_{\alpha}$ increases with gap (for similar
electrode configuration). Carroll et al. [6.12] suggested that the increase in O$_2$(a) production from the presence of NO in the discharge gas mixture that they first observed is due to a lower ionization potential of NO which leads to increased electron number density in the discharge promoting better discharge stability and increased pumping of the O$_2$(a) [6.12]. Braginsky et al. [6.5] expand on this idea by suggesting that the beneficial influence arises from the lower ionization potential gas mixture leading to the plasma occupying more volume within the gap, thus lowering the normal current density [6.5].

The normal current density corresponds to the minimum of the current-voltage characteristic (CVC) across the electrodes (including the quartz dielectric, the capacitive sheath, and the bulk plasma positive column (PC)). Assuming plane-parallel configuration (as in geometry #3, described in next subsection), and treating the quartz and sheath as capacitors (reactive elements) in series with the positive column (active element), the electrode voltage can be modeled as

$$V(J) = \left[ V_{s+q}^2 + V_{PC}^2 \right]^{1/2} = \left[ \left( \frac{d_\alpha + 2(d_q / \varepsilon_q)}{\varepsilon_0 \omega} J \right)^2 + (Cpd_\alpha J^{-m})^2 \right]^{1/2}, \quad \text{(Eqn. 6.1)}$$

where $V_{s+q}$ is the combined voltage across the sheath and quartz walls, $V_{PC}$ is the positive column voltage, $d_\alpha$ is the $\alpha$-mode sheath thickness, $d_q$ is the quartz thickness, and $d_1 = d - d_\alpha$ (PC gap); $C$ and $m > 0$ are constants dependent on the gas which describe the descending character of the PC CVC [6.10]. Eqn. 6.1 has a minimum, which corresponds to the normal current density,

$$J_{na} = \left( \frac{\varepsilon_0 \omega Cpd_\alpha \sqrt{m}}{d_\alpha + 2(d_q / \varepsilon_q)} \right)^{1/(m+1)}.$$

Experiments and 2-D modeling work by Rakhimova et al. [6.4] showed agreement with the basic model of Eqn. 6.2, establishing that increasing the frequency from 13.56 to 81 MHz (for an energy deposition range of 50-400 J/mmol) leads to higher normal mode current densities. The case modeled was 10 Torr of pure oxygen in a transverse discharge with 14-mm gap and 30-cm electrode length. At 13.56 MHz, the discharge glow filled the electrode gap, and the power was uniformly deposited [6.4]. In the 81 MHz case, the plasma did not fully occupy the discharge gap, and the discharge operated in normal current density mode [6.4]. In the modeling result, the length occupied by the 81 MHz discharge increased with
energy deposition, which was in good agreement with visual observation of the experiment [6.4]. Also, the electron density and specific energy input (per unit volume) in the 81 MHz case were twice as high as the 13.56 MHz case [6.4].

If the discharge is driven to higher current density by some means (for example, by increased power in an abnormal discharge), the secondary electron emissions (γ-processes) become significant at the electrode boundary, and transition from α to γ mode results. The transition is classically modeled as the breakdown of the α-mode sheath dictated by the Townsend condition. The Townsend condition for charge multiplication applied to the sheath with gap \( d_s \) is

\[
\gamma \left( \exp(\alpha d_s) - 1 \right) = 1, \tag{Eqn. 6.3}
\]

where \( \alpha \) is the ionization coefficient, and \( \gamma \) is the secondary emission coefficient. The relation in Eqn. 6.3 ensures that an electron emitted from the electrode region multiplies in the sheath field, generating enough ions to produce another electron due to secondary emission. The ionization coefficient is a function of the field (and pressure) in the sheath, \( \alpha = \alpha(p,E) \) (the typical form is \( \alpha = A \exp(-Bp/E) \) with \( A \) and \( B \) being experimentally determined constants), and therefore Eqn. 6.3 corresponds to a critical voltage \( V_t \) of the α-mode sheath breakdown [6.10]. This breakdown threshold is reached at a critical current density at which the maximum voltage across the sheath during the RF cycle reaches \( V_t \).

Based on this model of α-mode sheath breakdown, the critical current density has the form

\[
J_{cr} = e_v B \rho \omega \left[ \ln \left( 2A \left( \frac{eE}{m \nu_m} \right) \frac{p}{\omega} \right) - \ln \left( \ln \left( 1 + \gamma^{-1} \right) \right) \right]^{-1}. \tag{Eqn. 6.4}
\]

In Eqn. 6.4, \( B \) has units of \( \text{V-Torr}^{-1}\text{-m}^{-1} \), and \( A \) has units of \( \text{Torr}^{-1}\text{-m}^{-1} \). Based on this simple model of transition (Townsend condition), the current density that can be supported in α-mode (normal or abnormal) will be limited dependent on pressure, excitation frequency, the properties of the discharge gas (\( \nu_m, A, B, E/N \)), and the secondary emission coefficient which depends on the gas and emitting material (in this case, quartz dielectric).

Vidaud et al. [6.13] experimented with α to γ transition in nitrogen discharges between 10 and 100 Torr and found that transition voltage increases with increasing pressure, and decreases with increasing frequency. Odrobina and Kando [6.14] modeled the transition between α and γ mode in 1 Torr of argon and showed that increasing the applied frequency
led to a decrease in the sheath depth and delayed the transition to higher energy deposition, consistent with Rakhimova’s conclusions for the oxygen discharge [6.3]; Odrobina and Kando [6.14] also found that transition voltage decreased as frequency increased, consistent with the observations by Vidaud et al.

Equations 6.1-6.4, and the experimental works referenced above lay a framework for what parameters influence the behavior of a transverse RF discharge. For the application of O₂(a) production for an ElectricOIL, the best approach is to develop discharges which operate in a homogeneous normal (low-current density) α-mode. The experimental work to be described here demonstrates that especially pressure, frequency, and gap have a substantial influence on discharge behavior, and that efficient O₂(a) production can be optimized by proper selection of discharge parameters.

6.2. Transverse Discharge Configurations and Flow System

The results from a variety of transverse capacitive RF discharge geometries will be discussed. The plasma vessel configurations, power supplies, matching networks and diagnostic equipment used were described in detail in Sections 3 and 4. Figure 6.1 shows a sketch of the experimental setup used to measure O₂(a), O₂(b), and oxygen atoms in a variety of transverse RF configurations.

Figure 6.1. Sketch of experimental flow setup used to measure O₂(a), O₂(b), and oxygen atoms produced in a variety of transverse configurations: (1) circular flow channel “clamshell” with 4.9 cm maximum IG (internal gap), 479 cm³ IV (internal volume), (2) circular flow channel parallel plate with 4.9 cm IG, 479 cm³ IV, (3) rectangular flow channel parallel plate with 3.0 cm IG, 465 cm³ IV, (4) circular flow channel parallel plate with 2.0 cm IG, 77.4 cm³ IV, (5) circular flow channel parallel plate with 1.6 cm IG, 51.0 cm³ IV. For this study, all electrodes are 25.4 cm (10”) long in the flow direction.
6.3. Discussion of Transverse RF Discharge Modes and Electrical Characteristics

In work with the TCCRF discharges applied in ElectricOIL work, two mode transitions are of importance (1) normal to abnormal transition, and (2) homogeneous ($\alpha$-mode) to inhomogeneous ($\gamma$-mode) transition. In general, both of these transitions occur as the power (and therefore the current) of the discharge configuration is increased. Dependent on power level, pressure, flow rates, and excitation frequency it is possible for the discharge to operate in various combinations of these modes: normal-homogeneous, normal-inhomogeneous, abnormal-homogeneous, or abnormal-inhomogeneous. In some extreme cases (ex. high power to low flow rate ratio) the inhomogeneous plasma-jet type discharge described by Braginsky et al. [6.6, 6.7] was observed, but typically this corresponded to cases with extremely poor $O_2(a)$ production. So in this discussion, the term “inhomogeneous” will refer to the $\gamma$-mode as defined by Braginsky et al. [6.6] in which $\gamma$-processes (secondary electron emission from the wall near the electrode) become essential for maintaining the discharge. The normal mode behavior was observed visually, and by comparing the terminal (electrode) $V-I$ measurements and the observed volume of the plasma, some estimates of the normal current density were made. In the abnormal mode, the terminal CVC can be modeled using Eqn. 6.1, and based on this, the $E/N$ in the bulk plasma was estimated for typical laser-operation mixture of 10:33 $O_2$:He. The highest $O_2(a)$ production efficiencies ($\eta_{O_2(a)}$) are linked to the transition between normal and abnormal modes. Typically, $\eta_{O_2(a)}$ increases with power in the normal mode, and decreases with power in the abnormal mode. The influence of $\gamma$-processes is evidenced by increasing intensity of emissions at the electrode sheaths as power increases in the abnormal mode, and this is perhaps the reason for the significant decrease in $\eta_{O_2(a)}$ with power.

6.3.1. Visual Observations of Plasma Volume

The discharge volume can be observed by visual inspection of the various discharge glow emissions including the air-glow ($O + NO \rightarrow NO_2^* \rightarrow NO_2 + hv$) in the various cases with NO added to the flow. Figure 6.2 shows photographs of discharge geometry #2 driven at 13.56 MHz with a flow mixture of 10:33:0.15 $O_2$:He:NO at 20 and 50 Torr for varied power input. As the power is increased, the fraction of the plate gap occupied by the plasma emission is increased. For the 20 Torr case, with power increasing from 0.2 to 1 kW, the
plate gap is filled with homogeneous plasma at 400 W, and as more power is added (to 1 kW), bright emissions near the electrode are observed, indicating secondary emissions from the dielectric wall (γ-type processes); when the pressure is increased to 50 Torr, the plate gap is only half filled with plasma at 1 kW. The intensity on the centerline of the gap increases with flow distance, which may be due to higher dissociation near the walls (due to increased density of higher energy electrons), and the oxygen atoms diffusing into the center of the tube further downstream. Enlarged photographs of a few cases from Fig. 6.2 are shown in Fig. 6.3, in order to emphasize the transverse structure. The spatial behavior of the discharge in the smaller 2.0 cm diameter tube has some similarity to results for the 4.9 cm I.D. tube; as seen in Fig. 6.4, the visible plasma volume increases with power, and the plasma fills the electrode gap completely at 800 W RF at 50 Torr. The glow visible downstream of the discharge gap in Fig. 6.2 and 6.4 is due to O-NO recombination (air-glow).

Figure 6.2. Photographs of discharge glow in geometry #2 (circular, 4.9 cm diameter) at 13.56 MHz. The flow mixture is 10:33:0.15 mmol/s O₂:He:NO. The flow is from left to right. The pressure and RF power input for each case is listed below each photograph. These photographs were not taken with identical integration time.
The TCCRF discharge geometries #2 and #4 shown in Figs. 6.2 and 6.4 exhibit a normal current density effect similar to that described by Raizer [6.10] for moderate pressure discharges with coated electrodes. At low power setting, the discharges ignite at the downstream edge, and as power (current) is increased, the discharge volume increases, maintaining a nearly constant current density (normal mode). When the discharge volume is constricted by the plate geometry, as in Fig. 6.2, case (iii), the current density must increase, and the discharge becomes abnormal. As the current density increases, ion density in the sheath must increase, resulting in increased voltage amplitude across the sheath. At some critical current density, the sheath voltage reaches the threshold corresponding to the breakdown of the gas gap equal to the sheath thickness [6.10] The onset of the breakdown of the $\alpha$-mode sheath is evidenced by strong emissions due to secondary electrons near the dielectric surface where the copper plates contact the quartz tube (see Fig. 6.3,(ii)). Another key behavior to note is that as pressure increases, the plasma volume is reduced (for similar power input), and the discharge operates at higher power (and current) density, consistent with Eqn. 6.2. As will be shown in the following sub-sections, this behavior (which will be
referred to as pressure constriction) is also influenced by frequency, and this increased power density leads to decreased $O_2(a)$ production, and increased oxygen atom production.

**6.3.2. Current Voltage Characteristics (CVCs) of Transverse RF Discharges**

To show the transitions between modes in a typical EOIL discharge setup, the current-voltage-characteristic (CVC) was taken for discharge geometry #3 at the baseline flow rate of 10:33 $O_2$:He at ~20 Torr without, and with a trace NO flow rate of 0.15 mmol/s. As seen in Fig. 6.5.a, at low input powers, the discharge operates with normal current density with constant voltage as current increases. As power is increased, the current increases, and there is a transition from normal to abnormal in the neighborhood of 1.7-1.9 A, in which there is an initial drop in voltage, and then as power is increased further voltage and current both increase (abnormal behavior). As the current density is increased (due to the confinement of the plasma to the volume between the plates) the transition of the discharge from a homogeneous $\alpha$-mode to an inhomogeneous $\gamma$-mode is observed. The trace NO flow rate has little effect on the normal-abnormal transition point which occurs at approximately 350 W RF. However, the production of $O_2(a)$ increases significantly. Figure 6.5.b shows $[O_2(a)]$ determined from 1268-nm emission measured 58 cm downstream of the electrode gap for the cases in Fig. 6.5.a. In the normal $\alpha$-mode, $[O_2(a)]$ increases linearly with RF power; as more power is added, there is a (geometry-induced) transition to abnormal mode near 350 W input and the slope in $[O_2(a)]$ vs. RF decreases. The addition of NO results in an increase of the slope in $[O_2(a)]$ vs. RF in the $\alpha$-mode; the reason for this is not well understood, but is hypothesized to be due to the combination of three effects [6.15]: (1) shifting of the average $E/N$ (or $T_e$) to conditions more optimal for $O_2(a)$ production (original assumption, [6.16]), (2) improved electron-impact pumping of $O_2(a)$ due to conversion of oxygen atoms to ground state $O_2$, and (3) reduced kinetic quenching of $O_2(a)$ due to removal of oxygen atoms (and the associated buildup of ozone). Based on the similarities in terminal CVC without and with NO, it appears unlikely that this trace amount of NO has a substantial impact on the discharge $E/N$, which suggests that the beneficial increase in $O_2(a)$ production is due primarily to conversion of oxygen atoms to ground state $O_2$, or reduction of quenchers (Effects #2 and #3 above).
Figure 6.5. (a) Current-voltage characteristic and current-power characteristic and (b) [O$_2$(a)] measured 58 cm downstream of discharge for 10:33 O$_2$:He at ~21 Torr +/- 0.15 mmol/s NO in discharge geometry #3. The normal to abnormal transition occurs at ~350 W RF input in either case.

Figure 6.6 shows the influence of pressure on the CVC for 10:33 mmol/s O$_2$:He (no NO). As pressure is increased, the transition voltage and current both increase. For the 32 Torr case in Fig. 6.6, it was possible to operate the discharge in either normal or abnormal mode at powers near 500 W (2.8-3.4 A) by careful matching of the discharge as this transition point was approached from high (abnormal mode) or low (normal mode) powers; thus, a significant amount of overlap in the two modes is observed in the CVC. Figure 6.7 shows that the most efficient O$_2$(a) production occurs near the normal to abnormal transition point, although the best yield occurs at a higher power level (see for example Fig. 6.5.b.). The poor O$_2$(a) production efficiency in the low-power normal mode operation is due primarily to loses in the matching network as described in Section 3. In Fig. 6.8 the CVCs are shown for varied total flow rate at constant pressure. The CVC is not significantly influenced by the flow rate in comparison to the influence of pressure. The most efficient O$_2$(a) production occurs at low values of power deposition, $W < 50$ J/mmol, as seen in Fig. 6.9. The addition of NO in the 20 Torr case improves the peak O$_2$(a) efficiency from 16 % to 22%, but the peak efficiency is at similar power deposition ($W$ in J/mmol).
Figure 6.6. Current-voltage characteristic in discharge geometry #3 for 10:33 O$_2$:He with varied pressure. The transition voltage and current increase with increasing pressure.

Figure 6.7. O$_2$(a) production efficiency for discharge geometry #3 for 10:33 O$_2$:He with varied pressure. The transition current levels are denoted by the dashed vertical lines (increasing with pressure).

Figure 6.8. Current-voltage characteristic in discharge geometry #3 at 20 Torr with varied total flow rate (mmol/s) and constant O$_2$/He = 1/3.3.

Figure 6.9. O$_2$(a) production efficiency for discharge geometry #3 at 20 Torr with varied total flow rate (mmol/s) and constant O$_2$/He = 1/3.3. The peak O$_2$(a) yields in these cases are in parenthesis next to the flow rate.
The CVCs shown above establish that the normal to abnormal transition occurs as increasing power is deposited into the discharge, and that this transition influences O$_2$(a) production efficiency. From data in Fig. 6.6, it is obvious that pressure plays a significant role in determining the current (or power) level at which the transition will occur. Therefore, for a fixed power level and molar flow rate, it is possible to hold power input constant, sweep the pressure and observe the transition. The measured current density as a function of $pd$ (pressure*transverse gap) from TCCRF configurations #3 and #5 (described in Fig. 6.1) are shown in Fig. 6.10. The current density shown is the measured current divided by the effective electrode area determined by visual observation of the plasma glow; for abnormal cases the effective area is constant, while it decreases with $pd$ for the normal cases. The visually observed transitions between homogeneous ($\alpha$-mode) and inhomogeneous ($\gamma$-mode) discharges are indicated in Fig. 6.10. It is possible to have inhomogeneous discharge structure at both high and low pressure, which is associated with the critical current densities in both regimes (see for example Eqn. 6.4 which models the critical current density as a function of pressure, frequency, electrical parameters of the gas, and secondary emission coefficient).

![Figure 6.10. Current density as a function of ($pd = pressure*transverse gap$) for 10:33 mmol/s O$_2$:He. The solid vertical line at 120 Torr-cm marks the transition between abnormal and normal mode. Dashed lines indicate the visually observed transitions between homogeneous ($\alpha$) and inhomogeneous ($\gamma$) discharge structure. This does not account for stray current.](image-url)
6.3.3. Plasma Volume Measurements (using Herzberg I and II bands)

Visual inspection of photographs of the discharge (as in Figs. 6.2-6.4) is a good qualitative technique for discerning the volume occupied by the plasma between the plates, but does not adequately describe the discharge characteristics ($n_e$, $T_e$ or $E/N$). Also, interpretation of these photographs is difficult due to the presence of the airglow emission from O-NO recombination. In order to more adequately determine the influence of frequency on the discharge structure, the O$_2$(A$^3\Sigma \rightarrow X^3\Sigma$) and O$_2$(c$^1\Sigma \rightarrow X^3\Sigma$) transitions were monitored (Herzberg I and II band groups). A 404.7 nm filter with an 11-nm bandwidth was used, capturing a number of transitions in each band group. For fixed mixture and pressure, and assuming that the pumping rate is unaffected by frequency, the intensity of these states should be proportional to the electron density, and provide a qualitative representation of the discharge structure.

The 404.7 nm intensity measurement as a function of position and power from TCCRF discharge geometry #3, comparing 13.56 and 60 MHz at 20 Torr, is shown in Fig. 6.11.a. In these cases, the “filling” of the electrode gap proceeds in much the same way as was shown in Figs. 6.2 and 6.4 for geometries #2 and #4 respectively (normal current density effect). At low power, the discharge ignites at the downstream edge of the electrode gap, and spreads upstream as power is added. In the 60 MHz case, the power range of normal current density behavior is extended compared to the 13.56 MHz case. Figure 6.11.b shows some cross-sections of the data in Fig. 6.11.a along with similar data at 10 Torr for the same power to pressure ratio. The intensity plotted is the average of the filtered emission from three evenly spaced span-wise rows of 0.125” holes in the grounded electrode (see Section 4.1.3). In the 13.56 MHz case at 40 W/Torr, the visible plasma fills the electrode gap and the intensity is highest at the upstream side, falling off slowly with distance as the gas is heated and the oxygen is dissociated. For the same power per pressure input conditions at 60 MHz, there is no visible plasma in the upstream portion of the electrode gap; the intensity increases rapidly with distance beginning near the center of the gap and reaches a level higher than the 13.56 MHz case.
Figure 6.11. 404.7-nm intensity as a function of position and RF input power for varied excitation frequency in discharge geometry #3 (rectangular): (a) intensity as a function of position and RF input power for 10:33:0.15 mmol/s O₂:He:NO at 20 Torr, (b) intensity as a function of position for 10:33:0.15 mmol/s O₂:He:NO at 10 and 20 Torr with 40 W/Torr input RF power. The electrodes are 25.4 cm long in the flow direction.

This data indicates that increasing the frequency from 13.56 MHz to 60 MHz results in both higher electron density and higher current density (since the visible plasma fills only approximately the downstream half of the gap at higher frequency). In the lower pressure case (10 Torr), this effect results in enhanced O₂(a) production. At 20 Torr, there is no benefit in O₂(a) production for increased frequency, although the influence of frequency on discharge character is similar. The significant increase in electron density and decrease in plasma volume with frequency agrees well with modeling and experimental observations by Rakhimova et al. [6.4] which showed that increasing the frequency allows the discharge to operate in normal α-mode to higher energy deposition.

Figure 6.12 shows the intensity of the 404.7-nm emission as a function of height in the transverse gap for 13.56 MHz and 60 MHz at varied power input for 10:33:0.15 mmol/s at 20 Torr (conditions similar to Figs. 6.5 and 6.11.a). In the 13.56 MHz cases (Fig. 6.12.a), the transition between α-mode and γ-mode is observed as power increases. At 250 W, the intensity rises rapidly through the sheath at the dielectric surface, and is uniform through the gap. When the power is raised to 800 W (beyond the normal-abnormal transition point shown in Fig. 6.5) the intensity is fairly uniform, but there is an increase in intensity near the
walls, and evidence of a Faraday gap ("dark space") forming between the bright emission at the walls (negative glow, caused by energetic electrons leaving the sheath) and the bulk plasma (positive column). As the power is increased further (from 800 W to 1.6 kW), the bright negative glow regions near the walls grow in intensity, and the "dark" space becomes more pronounced.

![Graphs showing 404.7-nm intensity as a function of height in the gap (y) for varied RF input power in discharge geometry #3 (rectangular): (a) 13.56 MHz, and (b) 60 MHz. The flow conditions are 10:33:0.15 mmol/s O₂:He:NO at 20 Torr. The number in parentheses below the power level label on each curve is the intensity value by which the curve has been displaced above the y-axis; for example, the peak intensity in the 1.6 kW case in part (a) is ~150.](image)

In the 60 MHz cases (Fig. 6.12.b), the 404.7-nm intensity is more uniform than in the 13.56 MHz case. For 985 W input, the intensity at the boundary between the sheath and bulk plasma is only ~20% higher than the intensity in the center of the gap, and there is no evidence of a Faraday gap as in the 13.56 MHz cases at high power. The intensity profiles at 13.56 and 60 MHz for 800 W input are similar in shape, but the intensity at the centerline is approximately 40% higher in the 60 MHz case due to higher current density.

Figure 6.13 shows 404.7-nm filtered images of the transverse geometry #3 at 20 Torr, with varied RF power: (a) 250 W, where the discharge is normal homogeneous α-mode, (b)
800 W, where this discharge is abnormal near $\alpha$-$\gamma$ transition, and (c) 1.6 kW, where the discharge is in abnormal inhomogeneous $\gamma$-mode. Surface plots of 404.7-nm intensity for the same images in Fig. 6.13 are shown in Fig. 6.14 (the surface images shown correspond to a 5-cm long portion of the electrode gap which is 25.4 cm long in the flow direction). Figure 6.15 shows a filtered image and the corresponding surface plot for geometry #3 operating at 60 MHz, 800 W and 20 Torr, where the discharge is in normal homogeneous $\alpha$-mode. In Figs. 6.13-6.15 internal reflections of plasma emissions from the quartz wall are also observed.

Figure 6.13. 404.7-nm filtered images showing transverse structure of discharge in geometry #3 at 13.56 MHz, 20 Torr.
Figure 6.14. Surface plots of 404.7-nm intensity showing transverse structure of discharge in geometry #3 at 13.56 MHz: (a) 250 W (normal, $\alpha$-mode), (b) 800 W (abnormal, $\alpha$-$\gamma$ transition), (c) 1.6 kW (abnormal, $\gamma$-mode).
6.3.4. Calculation of $E/N$ using Terminal V-I Measurements

The abnormal CVC data in Fig. 6.6, along with the Eqn. 6.1 can be used to estimate the plasma positive column $E/N$, which is a vital parameter in determining the pumping of excited states in the discharge. The estimation is made by determining the positive column (PC) CVC $V_{PC}(J)$ and sheath thickness $d_\alpha$ which best fits the $V(J)$ data (terminal measurements), and then estimating the reduced electric field as $V_{PC}(J)/(d_1*N_{avg})$, where $d_1$ is the PC gap, and $N_{avg}$ is the average gas density in the discharge determined by the 762-nm spectra of O$_2$(b) taken within the discharge. The PC CVC is assumed to have the power dependence as shown in Eqn. 6.1, and $m$ is chosen by modeling the average discharge temperature data as $T_{avg}(J) = K*(J^m)$, where $K$ is a constant that increases with pressure. The modeling of the discharge CVC using Eqn. 6.1 is shown in Fig. 6.16. The $E/N$ determined from modeling the CVC is shown in Fig. 6.17; the $E/N$ values are between 20 and 25 Td (1 Td = 1x10$^{-17}$ V-cm$^2$). The normal current densities (minimum of $V(J)$ in Fig. 6.16) for the 10, 21, and 32 Torr cases are 1.8, 5.2, and 9.2 mA-cm$^2$ respectively, while the sheath thicknesses are 0.19, 0.11, and 0.092 cm respectively.
6.4. Excited State Production in Transverse Discharge

6.4.1. O$_2$(a) and O-atom results in baseline configuration (20, 30 and 50 Torr)

The O$_2$(a) produced within the discharge decays significantly with distance from the electrode gap due to the influence of oxygen atoms in the afterglow. Figure 6.18 shows the decay of O$_2$(a) yield in the afterglow of TCCRF discharge geometry #1 for operation at 800 W in a mixture of 10:33:0.15 mmol/s O$_2$:He:NO at 20, 30 and 50 Torr. The exit yields for these cases are ~16% at 20 Torr, ~14% at 30 Torr, and ~6% at 50 Torr; the slope of yield with distance is similar for the three pressures. This slow decay along the tube is influenced by three mechanisms in the afterglow of the discharge: (1) three-body deactivation mechanism O$_2$(a) + O$_2$ + O → 2O$_2$ + O, (2) quenching by oxygen atoms O$_2$(a) + O → O$_2$ + O, and (3) O$_2$(b$^1\Sigma$) deactivation by oxygen atoms, O$_2$(b) + O → O$_2$(a,X) + O. Modeling the observed decay using the rates provided by Palla [6.17] resulted in agreement within a factor of two, which is reasonable considering the uncertainty in the O$_2$(b) density, and the branching ratio of the quenching of O$_2$(b) to O$_2$(a). Due to these kinetics, the behavior of O$_2$(a) in the discharge afterglow is heavily dependent on the level of oxygen atoms in the system.

Figure 6.16. Comparison of the measured and calculated terminal CVC for geometry #3 flowing 10:33 mmol/s O$_2$:He with varied pressure. $J_{dis}$ is the rms current density calculated by dividing the discharge current by the electrode plate area, after accounting for a stray capacitance of 24 pF.

Figure 6.17. $E/N$ of the positive column determined from calculated CVC for geometry #3 flowing 10:33 mmol/s O$_2$:He with varied pressure.
Oxygen atoms are removed in the discharge afterglow primarily by reactions with NO and NO₂, and less rapidly through wall recombination. Figure 6.19 shows the decay of the oxygen atom yield with distance for the same conditions shown in Fig. 6.18; when the flow temperature data is used to adjust the [O] data as a function of flow time \( t \), the oxygen atom decay follows the dependence, \([O](t) = [O]_0 * \exp(-K_O * N * t)\), where \( N \) is the average gas density in the measurement region, \( K_O = 2.56 \times 10^{-16} \text{ cm}^3\text{s}^{-1} \) is a global decay rate, and \([O]_0 \) is the measured oxygen atom density at the most upstream point. This behavior agrees well with a two-body decay mechanism. The most likely mechanism is the fast titration reaction \( \text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 \). The NO₂ required for this mechanism can be produced by three-body recombination \( \text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M} \) as discussed in [6.18]. Based on the rates of these mechanisms, and the flow parameters for the data in Figs. 6.18 and 6.19, the two-body titration reaction will dominate the three-body recombination by an order of magnitude if the ratio of \([\text{NO}_2]/[\text{NO}]\) is greater than \( \sim 1 \times 10^{-2} \). Assuming this value, the decay can be reformulated as \([O](t) = [O]_0 * \exp(-k_{\text{titr}} * [\text{NO}_2] * t)\), where \( k_{\text{titr}} \) is the rate of the titration reaction \( \text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 \), and \([\text{NO}_2] \sim 1 \times 10^{-2} *[\text{NO}] = 1 \times 10^{-2} * ((10+33+0.15)/0.15)*N;\) thus, \( k_{\text{titr}} = K_O(100)(10+33+0.15)/0.15 = 7.4 \times 10^{-12} \text{ cm}^3\text{s}^{-1} \). Considering the approximations and
uncertainties involved, this is in good agreement with the established rate, 6.5x10^{-12} \times \exp(120/T) \text{ cm}^3\text{s}^{-1} which varies from 7.9x10^{-12} to 8.3x10^{-12} \text{ cm}^3\text{s}^{-1} over the measured temperature range for Figs. 6.18 and 6.19 (500-600 K) [6.19].

6.4.2. Influence of excitation frequency on O_2(a) and O-atom production

Figure 6.20 shows O_2(a) yield as a function of pressure without and with NO for 800 W RF input at 13.56 MHz and 60 MHz in TCCRF discharge #3 (rectangular tube, 3.0 cm gap). These measurements were made 89 cm downstream of the discharge gap in a 50-mm I.D. circular flow channel, and therefore the curves are distorted from the exit yield by increasing O_2(a) decay as pressure is increased. It was necessary to make measurements at this downstream location in order to have direct yield comparisons over the range of discharge tube geometries; the transition between the smaller diameter tubes and the 50-mm I.D. (well-calibrated) diagnostic block volume results in a subsonic jetting effect (highly visible via O-NO recombination emission) which confuses interpretation of the measured 1268-nm intensity due to axial variations of flow parameters. The addition of NO increases the O_2(a) production through the entire pressure range investigated. The influence of discharge excitation frequency on O_2(a) production as a function of pressure is substantial. At 5 Torr with NO added, the yield increases by more than a factor of two when frequency is increased from 13.56 to 60 MHz, reaching a maximum of 18%; near 20 Torr, the production level of O_2(a) is nearly identical at the two frequencies, despite the differences in volume and mode summarized in Figs. 6.11 and 6.12; at pressures greater than 20 Torr, the use of the higher frequency results in strong reduction in O_2(a) levels and it is better to use 13.56 MHz at $p > 20$ Torr for this particular geometry.

A hypothetical reasoning for the dependence of O_2(a) production on pressure and frequency observed in Fig. 6.20 is as follows. At low pressure and frequency, and sufficiently high power (800 W in this case), the discharge fills the plates and operates in abnormal $\gamma$-mode, where O_2(a) production efficiency is low due to the inhomogeneous structure: the inefficiency could be due to higher electron temperatures near the walls which favor higher energy processes such as dissociation over O_2(a) production. As pressure is raised, the plasma becomes more uniform, and transitions from an inhomogeneous $\gamma$-mode, to a homogeneous $\alpha$-mode, in which conditions are favorable for O_2(a) production, and the O_2(a)
yield increases. As pressure increases further, the discharge begins to constrict and operates in a normal current density α-mode (see Fig. 6.10); the constriction leads to increasing current density with pressure, producing conditions that are increasingly unfavorable for O₂(a) production and increasingly favorable for higher energy processes such as dissociation. As discussed in Section 6.1, and shown by plasma volume measurements in Section 6.3.3, increasing the excitation frequency from 13.56 to 60 MHz allows the normal mode discharge to operate at higher current density. Thus as pressure is swept for constant power (Fig. 6.20), the higher frequency discharge constricts to a smaller volume and higher normal current density as pressure is increased, transitioning from an abnormal discharge to a normal discharge at lower pressure.

![Figure 6.20. O₂(a) yield as a function of pressure for varied excitation frequency and NO flow rate in discharge geometry #3 (rectangular). Data measured 89 cm from discharge exit.](image)

![Figure 6.21. O₂(a) yield as a function of RF input power at 10 and 20 Torr for varied excitation frequency in discharge geometry #3 (rectangular). Data measured 89 cm from discharge exit.](image)

Figure 6.21 shows the influence of excitation frequency on O₂(a) yield as a function of power in discharge geometry #3 for 10:33:0.15 mmol/s O₂:He:NO at 10 and 20 Torr. The O₂(a) production is similar for the two frequencies at 20 Torr; at 10 Torr, the slope of yield with power is significantly increased for the 60 MHz case. For the 20 Torr cases, as evidenced by the intensity profiles in Figs. 6.11 and 6.12, the discharge is approximately homogeneous up to 1 kW for both 13.56 and 60 MHz, and this leads to similar production
efficiency of $O_2(a)$ for both frequencies. The lower residence time in the 60 MHz case is
balanced by the higher current density which results in more rapid pumping rates. For the 10
Torr cases, there is less similarity in the discharge structure: the 13.56 MHz case operates in
an abnormal mode throughout the sweep leading to the onset of $\gamma$-mode at $\sim$400 W which
saturates the $O_2(a)$ production, while the 60 MHz case begins in normal current density mode
at low power, fills the electrode gap at $\sim$500 W (becoming abnormal), and maintains a
homogeneous structure up to 1 kW. Thus maintaining a homogeneous discharge structure is
vital for efficient $O_2(a)$ production.

Increased frequency also results in a significant increase in oxygen atom production. The oxygen atom content determined by O-NO recombination emission at 580-nm is shown
in Fig. 6.22 as a function of RF input power at 10 and 20 Torr. At the measurement position
(46 cm from the exit), the oxygen atoms are nearly completely recombined for pressures of
30 Torr and greater (not shown). However, the increase in dissociation due to frequency is
substantial for the data at 10 and 20 Torr; increasing the frequency to 60 MHz results in the
discharge being either (1) shifted to a normal current density $\alpha$-mode from $\gamma$-mode (10 Torr
cases) or (2) constricted in $\alpha$-mode to higher current density operation (20 Torr cases). In
either situation, the current density is increased, and this results in increased oxygen
dissociation.

Figure 6.22. The influence of frequency on oxygen atom production. The airglow
emission due to O-NO recombination was measured as a function of power for varied
discharge frequency and pressure. The measurement was made 46 cm downstream
using a PMT filtered at 580 nm.
6.4.3. $O_2(a)$ and $O$-atom Production with pd-Scaling to Higher Pressures

Rahkimova et al. [6.4] observed improved $O_2(a)$ yield at 30 Torr by increasing excitation frequency from 13.56 MHz to 81 and 160 MHz, and decreasing the tube diameter from 14 mm to 7 mm, referring to this approach as “pd-scaling”. The purpose of increasing the frequency is to scale the sheath thickness of the discharge as the gap (or tube diameter) decreases; the sheath thickness should scale with the electron drift oscillation amplitude, and for electronegative gases should be inversely proportional to excitation frequency. In this work, decreasing the discharge gap (and volume) led to enhanced $O_2(a)$ production at midrange pressures (20-70 Torr). Figures 6.23 and 6.24 summarize data taken with discharge configuration #4 (circular, 2.0 cm gap) at varied excitation frequency. Although the behavior with pressure and frequency is similar to that seen in Fig. 6.20, the peak $O_2(a)$ production shifts to higher pressure; for the smaller diameter tube, the current density for homogeneous normal mode operation occurs at higher pressure (see pd scaling in Fig. 6.10), and conditions for optimal $O_2(a)$ production at high pressures are improved. At an operating pressure of 20 Torr, increasing the excitation frequency from 13.56 MHz to 60 MHz doubled the $O_2(a)$ production; $O_2(a)$ yield > 15% was obtained for the 60 MHz case. This improvement is likely due to a more homogeneous discharge induced by the increased frequency.

The increased frequency led to similar changes in oxygen atom production in both geometries #3 and #4; Fig. 6.25 compares actinometry measurements of oxygen atom yield for these two geometries operating at 13.56 and 60 MHz at 800 W. The significant increase in power density ($W/cm^3$) and decrease in residence time between geometries #3 and #4 results in a substantial increase in the dissociation. For geometry #3, the higher power density at 60 MHz compared to that at 13.56 MHz results in the slope of dissociation fraction increasing by nearly a factor of 6; in the smaller diameter tube (geometry #4) the slope of atom production at 13.56 and 60 MHz is similar, which is likely due to the power densities being similar in this case; however, the oxygen atom level is higher at the discharge exit for the 60 MHz case.

Figure 6.26 shows that the $O_2(a)$ yield was increased at high pressure by increasing the diluent ratio; ~13% yield was obtained at 50 Torr exciting the small diameter discharge (geometry #4) at 27 MHz. As was observed by Woodard et al. [6.2] for varied oxygen flow rates, the $O_2(a)$ yield saturates at a ratio of 6:1 He:$O_2$. Early work with EOILs [6.20]...
established that the use of helium diluent lowers the $E/N$ (electric field-to-gas density ratio) of the discharge, resulting in reduced electron temperatures which are more favorable for excitation of O$_2$(a) (which has a threshold of 0.98 eV). Some of the benefit with the addition of helium is likely due to the reduced residence time between the discharge and measurement point; as helium is added, the flow speeds up, and there is less flow time for O$_2$(a) to decay.

![Figure 6.23](image1.png)  
**Figure 6.23.** O$_2$(a) yield as a function of (diagnostic block) pressure for varied excitation frequency at 800 W in discharge geometry #4 (circular, small diameter). Data measured 89 cm downstream from the discharge exit. The cases to the left of the vertical line at ~3 Torr correspond to cases in which the discharge pressure is higher than the diagnostic block pressure.

![Figure 6.24](image2.png)  
**Figure 6.24.** O$_2$(a) yield as a function of power for varied excitation frequency at 20 Torr in discharge geometry #4 (circular, small diameter). Data measured 89 cm downstream from the discharge exit.

The addition of helium should also influence the modal behavior of the discharge. As discussed by Yatsenko [6.11], the critical boundary between $\alpha$ and $\gamma$ modes occurs at a significantly higher value of $pd$ (product of pressure and gap) for helium compared to air, nitrogen, and carbon-dioxide. Since the $\alpha\rightarrow\gamma$ transition is induced by breakdown of the capacitive $\alpha$-mode sheaths (dependent on the Townsend condition and first and second ionization coefficients [6.11]), it is reasonable to conclude that the lower ionization coefficient of helium leads to a delay in the transition to higher current density. However, the impact of helium diluent on discharge structure was not investigated in the present study.
Figure 6.25. Oxygen atom yield as a function of position inside the electrode gap in TCCRF discharge geometries #3 and #4 at 13.56 and 60 MHz. The flow conditions were 10:33:0.1 mmol/s \(O_2:He:NO\) at 20 Torr. The RF power input was 800 W. The oxygen atom yield was measured in the discharge using trace argon actinometry.

Figure 6.26. \(O_2(a)\) yield as a function of helium diluent flow rate for varied RF excitation frequency at 50 Torr in discharge geometry #4 (circular, small diameter) with 700 W RF input power and an input oxygen flow rate of 10 mmol/s. Data measured 89 cm downstream from the discharge exit.

6.5. Transverse Discharge Scaling Parameter for \(O_2(a)\) Production

The data in Section 6.3 demonstrates the influence of transverse discharge design parameters (pressure, gap, excitation frequency) on discharge behaviors (modes, volume, and electrical characteristics). The data in Section 6.4 demonstrates the influence of transverse discharge parameters on \(O_2(a)\) production. One basic conclusion can be drawn from this data: for a given transverse discharge geometry, operating at a particular frequency, power input, and flow rate, there is a particular operating pressure at which \(O_2(a)\) yield is maximized. The pressure at which \(O_2(a)\) yield is maximized changes dependent on geometry (gap) and excitation frequency: it shifts to lower (higher) pressure as frequency increases (decreases); it shifts to higher (lower) pressure as gap decreases (increases). This behavior comes about because of two types of constriction which occur in transverse RF discharge: (i) geometrical constriction, and (ii) pressure constriction. In the first case, geometrical constriction, the volume of the plasma is limited to the volume between the electrode plates, and is therefore abnormal (current density and voltage must rise with increased power input). In the second case, pressure constriction, the plasma volume is limited due to the ability of
the normal mode to operate at increased current density as pressure increases. Thus, as pressure increases, the transverse RF discharge goes through four mode combinations (1) abnormal-inhomogeneous, (2) abnormal-homogeneous, (3) normal-homogeneous, (4) normal-inhomogeneous (see for example Fig. 6.10). \(\text{O}_2(a)\) yield is maximized in homogeneous discharge (with highest efficiency in normal-homogeneous mode), and the pressure at which this condition is obtained depends characteristically on the gap and frequency. Based on the 1-D plane-parallel model given in Sect. 6.1 (Eqn. 6.2), the current density of the normal homogeneous \((\alpha)\) mode increases with the product of pressure, gap and frequency. This results in \(\text{O}_2(a)\) production efficiency being dependent on pressure, gap and frequency. A simple scaling factor is the product \(pdf\) \((\text{pressure} \times \text{gap} \times \text{frequency})\); \(\text{O}_2(a)\) yield is plotted versus \(pdf\) (units of Torr-cm-MHz) in Fig. 6.27 for varied configuration and frequency, showing that \(\text{O}_2(a)\) yield is maximized in the \(pdf\) range 750-2000. The same data is plotted in Fig. 6.28 (normalized to maximum measured value) versus an alternative scaling parameter, referred to here as the transverse scaling parameter \(TSP = (p^{2/3} \times d \times f^{1/3})\). \(\text{O}_2(a)\) yield is maximized in these cases for \(TSP \approx 50\). The data in Fig. 6.28 indicate that \(\text{O}_2(a)\) production can be maximized for a variety of transverse RF configurations (given gap, flow rate, and specific power \(W_{O_2}\)) by proper selection of pressure and frequency.

![Figure 6.27. \(\text{O}_2(a)\) yield versus the product \(pdf\) (pressure \(\times\) gap \(\times\) frequency) for varied pressure and discharge configuration. The power input is 800 W in all cases, and the flow rates are 10:33 \(\text{O}_2:He\) with trace NO, such that \(W_{O_2} = 80\) J/mmol. The electrode length is 25.4 cm in all cases.](image)

![Figure 6.28. Normalized \(\text{O}_2(a)\) yield versus \(TSP\) (transverse scaling parameter) for varied pressure and discharge configuration. The power input is 800 W in all cases, and the flow rates are 10:33 \(\text{O}_2:He\) with trace NO, such that \(W_{O_2} = 80\) J/mmol. The electrode length is 25.4 cm in all cases.](image)
6.6. Summary and Discussion

The region of high yield operation in an EOIL discharge was extended to higher pressures by following the $pd$-scaling laws exemplified by Rakhimova et al. [6.3, 6.4] and Braginsky et al. [6.5-6.7], showing improved operation by decreasing the electrode gap while increasing the excitation frequency. The transitions between transverse modes was established by CVC (current-voltage-characteristic) measurements and transverse intensity profiles in geometry #3 at 13.56 MHz; measurements of $O_2(a)$ in the afterglow clearly indicate the reduction in $O_2(a)$ production efficiency after normal-to-abnormal transition, although the peak yield occurred at higher energy deposition near the onset of $\gamma$-mode (Fig. 6.5). This saturation effect due to $\alpha \rightarrow \gamma$ transition is similar to that described in work at lower oxygen flow rates by Rakhimova et al. [6.3]. Intensity measurements in Fig. 6.11 indicate that changing the excitation frequency from 13.56 MHz to 60 MHz causes the discharge to operate in normal current density $\alpha$-mode to higher power inputs. However, this did not delay the saturation effect for the cases at 20 Torr, and nearly the same $O_2(a)$ yield performance was achieved between 0.2 and 1 kW at both 13.56 MHz and 60 MHz. At 10 Torr, the saturation effect was delayed to higher power input by increasing the frequency from 13.56 MHz to 60 MHz, and a significant improvement in peak $O_2(a)$ yield was observed (Fig. 6.18). This effect is likely due to the influence of frequency on the discharge mode: at 10 Torr, increasing the frequency converts the discharge from inhomogeneous $\gamma$-mode to homogeneous $\alpha$-mode throughout the power sweep (0.2-1 kW), while at 20 Torr, the discharge structure is nearly homogeneous throughout this power range, although there is onset of $\gamma$-mode in the 13.56 MHz case which becomes pronounced at ~800 W (Fig. 6.12.a). The increased intensities near the electrodes at higher powers (>800 W) indicate that a significant power loss is occurring in the sheaths due to processes associated with secondary electrons. Homogeneous $\alpha$-mode discharge offers the best $O_2(a)$ production efficiency, where the bulk of the power is dissipated uniformly in the gap.

A key issue that was demonstrated in this study is that the use of higher excitation frequency to induce $\alpha$-mode operation results in higher oxygen atom production (Fig. 6.22). This can be attributed to the higher current density operation due to the associated constriction of the discharge when it operates in normal $\alpha$-mode at 60 MHz (Figs. 6.11-12). For 800 W input at 20 Torr into geometry #3, the discharge constricted from filling the
electrode gap (at 13.56 MHz) to filling half the gap (at 60 MHz), and this resulted in a 6-fold increase in the slope of the oxygen atom yield within the discharge (Fig. 6.25). This is a discouraging result, considering oxygen atoms are a significant quencher of O_2(a) [6.3] and I* [6.16]; oxygen atoms were removed by NO and NO_2 in early work by Carroll et al. to reduce I* quenching, and were removed by catalytic reactions at an HgO-coated wall in work by Rakhimova et al. [6.3] in order to delay saturation of O_2(a) with power deposition. From O-NO recombination measurements it is obvious that the addition of NO is effective at removing oxygen atoms in the afterglow; however, the removal of oxygen atoms by reactions with NO is not sufficient to significantly reduce the buildup of oxygen atoms within the discharge for fast flow conditions, as shown by Woodard et al. [6.2]. When the increase of excitation frequency leads to constriction, higher current density results, and this tends to favor O-atom production over O_2(a). A similar problem occurred in work by Rakhimova et al. [6.3], where the HgO coating became less effective at delaying the saturation of O_2(a) with power as the discharge was operated at higher pressure and flow rate. Based on these effects, a high current density discharge should be avoided, because this leads to more rapid build-up of oxygen atoms which are a rapid quencher of O_2(a) and I*, leading to lower system efficiency when the discharge is applied to an EOIL.

Operating transverse RF discharges in a smaller tube at increased frequency led to improved O_2(a) production efficiency at higher pressures (20-70 Torr). At 20 Torr operation in discharge geometry #4, increasing the frequency from 13.56 MHz to 27 MHz and then to 60 MHz lead to incremental improvements in O_2(a) efficiency (Fig. 6.24). For these same conditions, there was not a significant change in oxygen atom production, due to the power density being similar in these cases (Fig. 6.25). The improved production due to increase frequency could be due to reduced sheath thickness, as first discussed by Rakhimova et al. [6.3] (the sheath thickness should be proportional to the electron drift oscillation amplitude). However, the oxygen atom production is increased from the levels obtained in the larger volume due to the increased power density (Fig. 6.25). Therefore, the oxygen atom production which influences O_2(a) saturation is not sufficiently suppressed by more rapid diffusion and recombination at the wall in the smaller diameter tube, and the oxygen recombination mechanisms with NO are less effective in this case due to the decreased residence time in the discharge [6.2]. If the O-atom production could be better suppressed, it
is likely that the high-pressure production of $O_2(a)$ could be improved, considering the modeling result that the $O_2(a)$ production efficiency should increase as $[O_2(a)]/[O_2(X)]$ is decreased [6.15]. However, the decrease in gap (diameter) in this case has allowed a homogeneous discharge to higher pressures, and $O_2(a)$ yield performance is improved as compared to the larger gap, larger volume discharges (for example geometries #1-3). The constriction of the discharge at high pressure (to high current density normal $\alpha$-mode) which was a concern in the large volume discharge is also a concern with the smaller diameter discharge (geometry #4), and this becomes more pronounced as the frequency is increased, because the normal $\alpha$-mode can support higher current density at higher frequency (see Eqn. 6.2). Thus better high-pressure performance was obtained at low frequency, because this allowed a lower current density discharge which favored $O_2(a)$ production.

References


7. The Influence of NOX on ElectricOIL Discharges

This section summarizes the experimentally observed influences of NO and NO2 on the ElectricOIL system. The discussion will be separated into four subjects: (i) the enhancement of O2(a) production, (ii) the removal of quenchers (O and O3), (iii) the influence of NOX on electrical parameters (E/N), and (iv) the NIR and UV emissions of NO excited states.

7.1. The Enhancement in O2(a) Production Due to NOX

As discussed in Section 5, the initial success of ElectricOIL was due to the introduction of NO2 to the system downstream of the discharge, in order to scavenge oxygen atoms which were quenching the upper laser state I* [7.1]. However, it was quickly discovered that adding NO either to the discharge flow or downstream of the discharge also enhanced O2(a) production significantly [7.1]. As described in Section 5, the initial reason for adding NO to the discharge flow mixture was to reduce the discharge E/N, which occurs due to NO having a significantly lower ionization potential than O2 and He (IP(NO) = 9.26 eV compared to IP(O2) = 12.07 eV, and IP(He) = 24.59 eV). The lowering of the electrode voltage due to NO was observed (Sect. 5), but the effect which NO has on O2(a) saturates with NO flow rate at a lower value than is required to make a significant impact on the electrode voltage. For example, with the 3-cm gap transverse discharge discussed in Section 6.3, the O2(a) production was maximized with a NO flow rate of 0.15 mmol/s added to 10:33 mmol/s O2:He, while the current-voltage-characteristic (CVC) was virtually identical with and without this amount of NO added. This behavior is typical, and is independent of discharge configuration (transverse, longitudinal hollow cathode, or inductive).

The influence of NOX on O2(a) levels downstream of the LCCRF discharge is shown in Fig. 7.1, giving three examples (i) NO2 injected downstream of the discharge, (ii) NO injected downstream of the discharge, and (iii) NO injected through the discharge. In the setup for this experiment (initially reported in [7.2]), the downstream injector was 15.24 cm downstream of the downstream hollow cathode, and the measurement was made 65.4 cm from the injection point. For these flow distances, the injection of either NO or NO2 downstream lead to approximately the same beneficial increase in O2(a) yield (~9.5 to
~12.5%, a significant 32% increase in magnitude), invariant after ~0.03 mmol/s NOX. Originally, it was supposed that this effect is due to the following process [7.2]:

**Step 1:** O$_2$(a) is produced due to branching of the fast exothermic reaction,

$$O + NO \rightarrow O_2(X,a,b) + NO \quad (R. \ 7.1)$$

**Step 2:** NO$_2$ lost in Step 1 is reproduced by 3-body recombination,

$$O + NO + M \rightarrow NO_2 + M, \ M = O_2, \ He \quad (R. \ 7.2)$$

The branching of Reaction 7.1 was investigated by Azyazov et al. using photolysis of NO$_2$, both at 248 nm which results in only O($^3P$) (ground state), and at 193 nm which results in both O($^3P$) and O($^1D$) with branching fractions of 0.45 and 0.55 respectively [7.3]. No formation of O$_2$(a) was detected in either photolysis experiment, and from the sensitivity of the experimental apparatus it was established that the branching of R. 7.1 into O$_2$(a) had an upper bound of <0.1. Thus, it was concluded that the production of O$_2$(a) from R. 7.1 is insignificant. Therefore, it is reasonable to conclude that the increase of O$_2$(a) is due to a reduced deactivation rate caused by reduction of quenching by suppressing both O-atoms and O$_3$ buildup (see discussion in Sect. 2.4.1). The influence of NO on these quenching mechanisms was also observed in the recent experiments by Ionin et al. [7.4] in which O$_2$(a) production in a pulsed electric discharge in CO:O$_2$:He mixture was studied. In those experiments, the addition of NO to the pulsed discharge mixture (at 0.1-0.3% of the O$_2$) greatly increased the lifetime of O$_2$(a) after the discharge pulse [7.4].

With similar amounts of NO passed through the discharge instead of being injected downstream (see again Fig. 7.1), the yield was increased to about 16% (a 68% increase in magnitude from the zero NO case!). The cause for this additional boost in O$_2$(a) is a subject of considerable speculation, and is likely a combination of less O$_2$(a) quenching due to suppression of O and O$_3$, and the effects of NO on discharge dynamics.
Figure 7.1. The effect of NO \_X injection on O\_2(a) yield in 3:16 mmol/s O\_2:He at 12.5 Torr, with 500 W RF [7.2]. The discharge used was LCCRF (hollow cathodes) with 25.4 cm gap.

Figure 7.2 shows spatial measurements of O\_2(a) within the hollow cathode RF discharge gap and in the region downstream of the electrode gap without and with a small amount of NO added to the O\_2:He flow mixture. This data was originally reported in [7.5], and was representative of typical discharge conditions for laser operation. Although it was not possible to make proper O\_2(a) measurements at 1268 nm in the discharge gap in the cases with NO due to NO(C\_A\_A) emissions, it is clear based on the data taken in the downstream region that the production of O\_2(a) within the discharge was improved significantly in both cases. Also, the decay of O\_2(a) with distance was slowed with NO (the O\_2(a) density increases with distance while temperature decreases such that O\_2(a) yield still decreases, but at a slower rate). Figure 7.3 shows spatial measurements of O\_2(b) density for the same cases in Fig. 7.2. The O\_2(b) density within the discharge is similar without and with trace NO, but in the downstream region the O\_2(b) decay is slowed in the presence of NO. Additionally, with trace NO added, the temperature increased by about 40 K at the discharge exit (565 K to 605 K in the 3 mmol/s O\_2 case, and 490 K to 530 K in the 10 mmol/s O\_2 case).

Thus, the presence of NO in the flow mixture both boosts the O\_2(a) production in the discharge, and improves the lifetime of O\_2(a) and O\_2(b) in the downstream region. However, from the spatial data taken at these conditions, it can be concluded that the primary benefit, the increase of O\_2(a) density, comes from the impact of NO on the discharge region kinetics.
7.2. The Reduction of Quenching Mechanisms by NOX

From the measurements in Figs. 7.1-7.3, it is obvious that the lifetimes of O2(a) and O2(b) are affected by NO or NO2 added to the system. This is because of the fast removal of O-atoms by NO2 titration (R. 7.1, k7.1 = 6.5x10^{-12}\exp(120/T) \text{ cm}^3/\text{s}), and the recycling of NO2 from NO by 3-body recombination (R. 7.2). The O-atoms are a rapid quencher of O2(a) by 2-body (R. 2.7) and 3-body (R. 2.8) deactivation, and also lead to the buildup of ozone by 3-body recombination of O and O2. Ozone is also a rapid quencher of O2(a) and O2(b), and therefore delaying its buildup by removing O-atoms in the post-discharge region contributes to an improved O2(a) lifetime.

7.2.1. Decay of O-atoms by NOX

The kinetics of O-atom removal by NO and NO2 are well established by the work of various researchers in atmospheric chemistry, for example the works of Kaufman [7.6] or Piper et al. [7.7]. A great deal of research has described the airglow kinetics dependent on pressure, background gas, and emission wavelength, and this has led to a reliable use of the airglow caused by O-NO recombination as a standard for O-atom measurement in the afterglow of ElectricOIL discharges. This diagnostic is especially useful considering that the
flow mixtures ideal for ElectricOIL performance (for example 10:33:0.15 O₂:He:NO) already include a known trace amount of NO, allowing quick, direct measurements of O-atom density downstream of the discharge using the calibrated PMT method provided by Piper et al. [7.7].

Using calibrated O-NO airglow measurements and NO₂ titration, it was possible to determine the level of O-atoms for conditions similar to those shown in Fig. 7.1. Figure 7.4 shows O-atom measurements taken downstream of a longitudinal hollow cathode RF discharge operating at (a) 12.5 Torr and (b) 20 Torr for three conditions: (i) no NO injection, (ii) NO injection downstream of the discharge (at 42 cm), and (iii) NO injected upstream (pre-mixed). The flow rates through the discharge were 3:16 mmol/s O₂:He and the input RF power was 500 W. The calibrated O-NO airglow method allows for the measurement of the decay of O-atoms downstream of the discharge (with NO in the flow) while the NO₂ titration method allows (one-point) measurement of the O-atoms when NO was not included in the flow mixture. The data are compared to BLAZE model calculations for the same flow conditions.

![Figure 7.4](image.png)

Figure 7.4. O-atom density measured downstream of a 13.56 MHz hollow cathode LCCRF discharge operating at (a) 12.5 Torr, (b) 20 Torr. The input RF power was 500 W. The flow rates were 3:16 mmol/s O₂:He, with 0.2 mmol/s NO added.

The introduction of trace NO either upstream or downstream of the discharge chamber results in a significant decrease in the downstream O-atom density due to the influence of R. 7.1 and R. 7.2, which speed up the O-atom recombination. The influence of these reactions
is well-illustrated by the BLAZE modeling. When the pressure is increased from 12.5 to 20 Torr, the O-atom decay rate increases due to the increase in the contribution of three-body kinetics. The BLAZE modeling well replicates the behavior in the 12.5 Torr case; in the 20 Torr case the modeled decay rate is similar to the data, but the model result appears shifted (in position) compared to the data. This shift may be due to the assumption in the modeling that a significant amount of power is deposited upstream of the hollow cathodes. However, in experiment, visible observations of the plasma glow suggest that the power deposition distribution changes as a function of pressure, with the plasma becoming more confined to the hollow cathode gap as pressure increases. Figure 7.5 shows O-atom density measurements with varied NO flow rate where the NO is (a) pre-mixed with the discharge gases, and (b) injected downstream of the discharge. Clearly, NO injected either pre-mixed or injected downstream can be used to rapidly recombine the atoms formed within the discharge.

Figure 7.5. O-atom density measured downstream of a 13.56 MHz hollow cathode LCCRF discharge with varied NO: (a) NO pre-mixed with discharge gases, (b) NO injected downstream. The input RF power was 500 W. The flow rates were 3:16 mmol/s O₂:He at 20 Torr.

Figure 7.6 shows the O₂(a) yield measured for the conditions shown in Fig. 7.5. Injection of NO downstream slows the decay of O₂(a). When NO is instead passed through the discharge, the O₂(a) yield in this case is improved by approximately 50%, with maximum
effect occurring at low NO flow rate, about 5% of the O\textsubscript{2} input flow rate. Thus when NO is used to increase O-atom recombination in the discharge region, the pumping of O\textsubscript{2}(a) is improved significantly.

![Figure 7.6](image)

**Figure 7.6.** O\textsubscript{2}(a) yield measured downstream of a 13.56 MHz hollow cathode LCCRF discharge with varied NO. Cases with pre-mixed NO and NO injected downstream (at 42 cm) are shown. Conditions match those of Fig. 7.5.

### 7.2.2. Ozone Buildup

Ozone is produced due to detachment mechanisms (e.g. O + O\textsubscript{2} \rightarrow O\textsubscript{3} + e\textsuperscript{-}) and O + O\textsubscript{2} recombination. In the post-discharge region, ozone is formed by 3-body recombination,

\[
O + O\textsubscript{2} + M \rightarrow O\textsubscript{3} + M, \quad M = O\textsubscript{2}, \text{He, etc.}
\]  

The rate for R. 7.3 applied in BLAZE modeling is \( k_{7.3} = 5.19 \times 10^{-27} T^{-2.8} \text{ cm}^6/\text{s} \), taken from Atkinson *et al.* [7.8]. Once formed, ozone quenches singlet oxygen states by reactions,

\[
O\textsubscript{2}(a) + O\textsubscript{3} \rightarrow O + 2 \text{O}_{2}(X), \quad k_{7.4} = 5.2 \times 10^{-11}\exp(-2840/T)
\]  

\[
O\textsubscript{2}(b) + O\textsubscript{3} \rightarrow O + 2 \text{O}_{2}(X), \quad k_{7.5} = 1.53 \times 10^{-11} \text{ cm}^3/\text{s}
\]  

\[
O\textsubscript{2}(b) + O\textsubscript{3} \rightarrow \text{O}_{2}(X) + O\textsubscript{3}, \quad k_{7.6} = 3.3 \times 10^{-12} \text{ cm}^3/\text{s}
\]  

\[
O\textsubscript{2}(b) + O\textsubscript{3} \rightarrow O\textsubscript{2}(a) + O\textsubscript{3}, \quad k_{7.7} = 3.3 \times 10^{-12} \text{ cm}^3/\text{s}
\]

The rates applied in BLAZE modeling are shown along with Reactions 7.4-7.7, taken from [7.8]; the branching applied for R. 7.5-7.7 is taken from the total rate of \( 2.2 \times 10^{-11} \text{ cm}^3/\text{s} \), the rate for \( k_{7.5} \) shown (from [7.8]), and assuming the remainder of the rate is split evenly between \( k_{7.6} \) and \( k_{7.7} \). The deactivation of O\textsubscript{2}(a) by O\textsubscript{3} is significantly slower than O\textsubscript{2}(b).
deactivation mechanisms by $O_3$, with a room temperature value of $k_{7.4}(300K) = 4.0 \times 10^{-15}$ cm$^3$/s (increasing significantly with temperature according to the temperature dependence measured in the range 280-360 K, 11 times faster at 400 K, and 114 times faster at 600 K). However, $R.7.4$ is relatively fast compared to other $O_2(a)$ deactivation mechanisms, and can therefore be influential dependent on the $O_3$ density. A typical rate for the reaction $O_2(a) + M \rightarrow O_2(X) + M$ would be $\sim 1 \times 10^{-18}$ cm$^3$/s [7.8]. For reference, various 2-body and 3-body $O_2(a)$ quenching mechanisms are compared to $R.7.4$ in Table 7.1, and the contribution to the $O_2(a)$ deactivation rate due to each mechanism is calculated for some sample flow conditions similar to those used in early ElectricOIL work. From this comparison, $R.7.4$ can be a significant mechanism, comparable to the 3-body loss of $R.2.8$, if $[O_3]$ is similar to the reasonable level assumed in the calculation (and assuming the temperature dependence is valid at higher temperatures).

### Table 7.1. Comparison of $O_2(a)$ quenching mechanisms.

<table>
<thead>
<tr>
<th>Type</th>
<th>Reaction</th>
<th>$k_i$ @ 450 K</th>
<th>$(d[O_2(a)]/dt)_i$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pooling</td>
<td>$2 : O_2(a) \rightarrow O_2(X) + O_2(b)$</td>
<td>$5.61 \times 10^{-17}$</td>
<td>$1.0 \times 10^{15}$</td>
<td>[7.9]</td>
</tr>
<tr>
<td>Self-deactivation</td>
<td>$2 : O_2(a) \rightarrow 2 : O_2(X)$</td>
<td>$1.69 \times 10^{-17}$</td>
<td>$3.0 \times 10^{14}$</td>
<td>[7.9]</td>
</tr>
<tr>
<td>He, 2-body</td>
<td>$O_2(a) + He \rightarrow O_2(X) + He$</td>
<td>$8.00 \times 10^{-24}$</td>
<td>$7.7 \times 10^{12}$</td>
<td>[7.9]</td>
</tr>
<tr>
<td>$O_2$, 2-body</td>
<td>$O_2(a) + O_2(X) \rightarrow 2 : O_2(X)$</td>
<td>$8.21 \times 10^{-19}$</td>
<td>$1.2 \times 10^{14}$</td>
<td>[7.10]</td>
</tr>
<tr>
<td>O-atom, 2-body ($R.2.7$)</td>
<td>$O_2(a) + O \rightarrow O_2(X) + O$</td>
<td>$1.99 \times 10^{-16}$</td>
<td>$7.2 \times 10^{13}$</td>
<td>[7.11]</td>
</tr>
<tr>
<td>O-atom, 3-body ($R.2.8$)</td>
<td>$O_2(a) + O_2(X) + O \rightarrow 2 : O_2(X) + O$</td>
<td>$1.00 \times 10^{-16}$</td>
<td>$1.2 \times 10^{16}$</td>
<td>[7.12]</td>
</tr>
<tr>
<td>$O_3$, 2-body ($R.7.4$)</td>
<td>$O_2(a) + O_3 \rightarrow O_2(X) + O_3$</td>
<td>$9.44 \times 10^{-14}$</td>
<td>$2.0 \times 10^{16}$</td>
<td>[7.8]</td>
</tr>
</tbody>
</table>

It follows from the $O_2(a)$ loss rate calculations in Table 7.1 that small levels of ozone could substantially influence the $O_2(a)$ quenching kinetics downstream of the discharge. For this reason, the PSI $O_3$ Microabsorbance detector was used to measure ozone buildup downstream of the discharge, and the influence of NO on ozone levels. Figure 7.7 plots $[O_3]$ measurements as a function of position for the same conditions shown in Fig. 7.2. The results are compared to the BLAZE model. For the cases without NO, the $[O_3]$ level at the measurement location is in the neighborhood of $1 \times 10^{14}$ cm$^3$, increasing with distance from the discharge gap. For the cases with NO added to the discharge flow, the $[O_3]$ was below the detection limit of the $O_3$ Microabsorbance detector ($< 1 \times 10^{12}$ cm$^3$), which is in good agreement with the predictions of the BLAZE model. The NO added to the discharge flow reduces the O-atom production, increases the O-atom decay in the post-discharge region, and
this leads to insignificant O₃ buildup in the post-discharge region. Therefore, the influence of R. 7.4 is reduced by more than a factor of 100.

Figure 7.7. Ozone density versus position with hollow cathode LCCRF discharge. Flow rates are in mmol/s. In the 3 mmol/s O₂ case, the RFsys = 450 W, p = 12.5 Torr. In the 10 mmol/s O₂ case, the RFsys = 550 W, p = 16.5 Torr. This model comparison with data was originally reported in [7.5].

7.2.3. O-atom Measurements with NO in the Discharge Region

Trace Argon Actinometry (TAA) was applied within the primary discharge in order to determine the influence of NO on the buildup of O-atom density along the discharge length. As discussed in Section 6, the buildup of O-atoms in the discharge is influenced by power density and residence time within the discharge; for example, a shorter, higher power density 60 MHz discharge had significantly faster O-atom buildup with distance than a longer 13.56 MHz discharge operating at the same input power. This makes sense considering that (to first order) \( \frac{d[O]}{dt} \sim k_{\text{diss}}n_e[O₂] \), and therefore a higher power density discharge having a higher electron density will produce O-atoms at a faster rate. The dissociation of O₂ by electron impact is countered by O-atom recombination mechanisms. In the shorter 60 MHz discharge, there was less flow time for the O-atoms to recombine, and this coupled with higher power density resulted in a higher dissociation fraction at the exit compared to the 13.56 MHz case.

The introduction of NO to the discharge adds competing O-atom recombination mechanisms to those already present in the O₂:He discharge. By increasing the O-atom conversion rate to O₂(X), the O₂(a) density allowed by the discharge electrodynamics is larger (see Sect. 2.3), and higher pumping efficiency into O₂(a) is achieved. When the
geometry and power density of the discharge change, despite similar total power input and gas mixture, the level of O$_2$ dissociation changes, because the balance between production (electron-impact) and loss mechanisms (recombination) is altered. This effect was observed when comparing TAA measurements in transverse discharges with varied gap and power density.

Figure 7.8 shows TAA results for three discharge configurations operating at 800 W RF with 10:33 mmol/s O$_2$:He, (a) without NO, and (b) with 0.3 mmol/s NO (these correspond to TCCRF discharges #3, #4, and #5 in Fig. 6.1). As the discharge volume decreases (Fig. 7.8.a), the power density increases, and this corresponds to a marginal increase in O-atom production, but given that power per flow rate of O$_2$ (specific power deposition) is constant, the level of atoms produced along the discharge tube is similar.

When 0.3 mmol/s is added (Fig. 7.8.b) the effect on O-atom production varies significantly dependent on configuration. In the lowest power deposition case at 1.75 W-cm$^{-3}$ (#3), [O]/[O$_2$]$_{inp}$ decreases substantially from 0.19 to 0.13 near the exit. In the 10.3 W-cm$^{-3}$ case (#4), the production along the tube is virtually unchanged, decreasing slightly towards the exit. In the 15.7 W-cm$^{-3}$ case (#5), the O-atom production increases slightly. This tradeoff between O-atom production and power deposition occurs because the balance between electron impact dissociation and O-atom recombination is altered. All three cases are at 20 Torr.

Figure 7.8. [O]/[O$_2$]$_{inp}$ as a function of position as power density increases due to change in discharge configuration: (a) no NO, (b) 0.3 mmol/s NO. The input flow rates are 10:33 O$_2$:He at 20 Torr. The input power is 800 W at 13.56 MHz in all cases.
Torr, such that three-body recombination with NO has similar influence (rate proportional to $k_{7.2}[O][NO][M]$). However, as the volume of the discharge decreases, the power deposition (W-cm$^{-3}$) increases, and assuming that the discharge maintains a similar $E/N$, the current density and electron density increase. Therefore, the dissociation rate increases (proportional to $k_{\text{dis}}n_e[O_2]$). Thus, as power density increases, the ratio of dissociation to recombination increases, and recombination mechanisms associated with NO become less effective. This effect is mimicked by the BLAZE model discharge kinetics; Figure 7.9 shows $O_2(a)$ yield and $O_2$ dissociation fraction as a function of NO flow rate. When power deposition (W-cm$^{-3}$) is increased the influence of NO on $O_2(a)$ and O-atoms produced becomes small.

![Figure 7.9. BLAZE model result comparing $O_2(a)$ and O-atom yield as a function of NO flow rate with varied power density (from Palla [7.13]). The 1-D steady-state calculation assumes $E/N = 20$ Td and $T = 300$ K (constant). For the 2 W-cm$^{-3}$ case $n_e ~ 1.6 \times 10^{10}$, and for the 14 W-cm$^{-3}$ case $n_e ~ 9.3 \times 10^{10}$.](image)

7.3. The Influence of NO on Electrical Parameters

It is easy to establish that the addition of NO to the O$_2$:He discharge flow mixture does lower the operating $E/N$. This is evidenced by a significant decrease in the electrode voltage as NO is added (see Fig. 5.5). However, it is difficult to say that this is the true reason why $O_2(a)$ production is enhanced by trace NO. To the contrary, modeling suggests that best $O_2(a)$ production is found by increased $E/N$ as $O_2(a)$ builds up in the discharge (see Sect. 2.3).

Some spectral measurements of excited atomic species within the discharge have suggested that the EEDF does change, suggesting a lower $E/N$ even with small amounts of NO. As was described in Section 4.4.4, two methods for determining $E/N$ values from the ratios of excited state emissions were investigated. The first deduces $E/N$ from the ratio of
O(3p\(^5\)P) 777-nm emission to the O(3p\(^3\)P) 844-nm emission which is the method that was applied by Pagnon et al. [7.14] (in DC discharge), and the second method deduces \(E/N\) by comparing the ratio of Ar(2p) emissions (due to trace Ar added for TAA). Although both line ratios were observed to change measurably with NO addition, developing a simplified collision-radiative model for relating the measured line ratios to \(E/N\) proved to be difficult.

An alternative method for optically measuring \(E/N\) using combination of Ar and Ne lines is suggested.

### 7.3.1. Measurements of Excited Oxygen Atom Line Ratios

The method applied by Pagnon et al. [7.14] relates the plasma \(E/N\) to the ratio of the O(\(^3\)P\(\rightarrow\)\(^3\)S) emission at 844 nm to the O(\(^5\)P\(\rightarrow\)\(^5\)S) emission at 777 nm. Using the form of Eqn. 4.13 to model the intensities of the two emissions, results in the relation

\[
\frac{I_{844}}{I_{777}} = C_{844/777} \frac{h \nu_{844} A_{844}^{3P} \sum k_{3P}^{e} \left[ Q_{m} \right]}{h \nu_{777} A_{777}^{5P} \sum k_{5P}^{e} \left[ Q_{m} \right]} \left( \frac{k_{844}^{3P}}{k_{777}^{3P}} \right),
\]

(Eqn. 7.1)

In Eqn. 7.1, the parameter \(C_{844/777}\) is the relative detector efficiency for the two emission measurements, and all other parameters are as defined in Sect. 4.4.2; superscript “3P” denotes the upper state of the 844 nm emission, and superscript “5P” denotes the upper state of the 777 nm emission. Pagnon et al. [7.14] applied this to measurements in a DC discharge operating at 1 Torr in the 10-100 mA range, and found good agreement with measured values (within 20%).

This method has been investigated for application to ElectricOIL RF discharges in O\(_2\):He:NO mixtures. The ratio \(I_{844}/I_{777}\) was measured using the Ocean Optics NIR USB4000 spectrometer discussed in Sect. 4.1. Measurements of the O-atom line intensity ratio \(I_{844}/I_{777}\) made in a 3-cm gap TCCRF discharge are shown in Fig. 7.10, showing cases with varied NO and excitation frequency. For the 60 MHz case, the discharge operates in normal mode, and the plates are only partially filled with visible (emitting) plasma; for the 13.56 MHz case the discharge operates in abnormal mode, and the plates are filled with visible plasma. The electron-impact cross-sections for O(\(^3\)P) and O(\(^5\)P) were shown in Fig. 4.16 (from Laher et al. [4.28]). Using these cross-sections along with EEDFs from the Globalkin Boltzmann model [7.15] for 10:33 O\(_2\):He in Eqn. 4.15 \((k_{ij} = \int_{\varepsilon_{a}}^{\varepsilon} \sigma_{ij}(\varepsilon) \nu(\varepsilon) F(\varepsilon) d\varepsilon)\) results in the electron
impact pumping rates shown in Fig. 7.11. Based on this calculation, the ratio of pumping rates $R_{3p/5p} = k_{e^{-}}^{3p}/k_{e^{-}}^{5p}$ increases from 0.86 to 2.4 over the range 6-60 Td.

![Figure 7.10. Measurements of the ratio $I_{844/777}$ made along the length of a 3-cm gap rectangular cross-section TCCRF discharge with varied NO (0, 0.1, 0.3 mmol/s), and frequency (13.56, 60 MHz). The flow conditions are 20 Torr, 10:33 mmol/s O₂:He, and the RF input is 800 W.](image1)

![Figure 7.11. Electron impact rates for direct excitation of O($3p^{5}P$) (777 nm) and O($3p^{3}P$) (844 nm), and the ratio $I_{844}/I_{777}$ as a function of E/N. The calculation was made using EEDFs from Globalkin model for a 10:33 O₂:He mixture at 20 Torr.](image2)

The relative detector efficiency $C_{844/777} = 0.617$ was determined using an Ocean Optics LS-1-CAL calibrated tungsten source. Using $C_{844/777}$ and $R_{3p/5p}$ in Eqn. 7.1 along with the quenching rates for O₂ from [7.14] yields the calculated values of $I_{844}/I_{777}$ shown in Fig. 7.11 at 20 Torr as a function of $E/N$. The measured values in Fig. 7.10 are significantly lower than the range of values produced in the calculation. From other analyses (terminal characteristics, microwave interferometer), the expected $E/N$ is approximately 20 Td; the calculated value for $I_{844}/I_{777}$ at 20 Td is higher than the measured value (no NO, 13.56 MHz case) by approximately a factor of 3.5.

### 7.3.2. Measurements of Excited Argon Atom Line Ratios

The ratios of atomic argon lines from the 2p manifold (from trace Ar introduced for actinometry) are also observed to vary when NO is introduced. Figure 7.13 shows the measured ratio of $I_{751.5}/I_{750.4}$ along the flow axis of a 3-cm gap TCCRF discharge; the ratio decreases with NO, but remains in the range of 0.3 to 0.36.
Figure 7.12. Measurements of the ratio \( I_{751.5}/I_{750.4} \) made along the length of a 3-cm gap rectangular cross-section TCCRF discharge with varied NO (0, 0.1, 0.3 mmol/s) at 13.56 MHz. The flow conditions are 20 Torr, 10:33 mmol/s O\(_2\):He, and the RF input is 800 W.

Figure 7.13. Electron impact rates for direct excitation of Ar(2p\(_1\)) (750.4 nm) and Ar(2p\(_2\)) (751.5 nm), and the corresponding calculated ratio of \( I_{751.5}/I_{750.4} \) as a function of \( E/N \). The calculation was made using EEDFs from Globalkin model for a 10:33 O\(_2\):He mixture at 20 Torr.

The pumping rates of the emitting states in Fig. 7.12, Ar(2p\(_1\)) at 750.4 nm and Ar(2p\(_2\)) at 751.5 nm, are shown in Fig. 7.13. The calculated intensity ratio using Eqn. 7.2 is also shown \((C_{751.5/750.4} = 1)\).

\[
\frac{I_{751.5}}{I_{750.4}} = C_{751.5/750.4} \frac{h \nu_{751.5} A_y^{2p5} \sum_k A_{ik}^{2p1} + \sum_m k_m^{2p1} \left[ \frac{Q_m}{Q_m} \right] \left( k_e^{2p1} \right)}{h \nu_{750.4} A_y^{2p5} \sum_k A_{ik}^{2p5} + \sum_m k_m^{2p5} \left[ \frac{Q_m}{Q_m} \right] \left( k_e^{2p1} \right)} \frac{k_e^{2p5}}{k_e^{2p1}} = f \left( \frac{E}{N} \right) \quad \text{(Eqn. 7.2)}
\]

The calculation uses the Ar(2p) cross-sections, spontaneous emission rates and quenching rates listed in Sect. 4.4 along with EEDFs determined using the Globalkin Boltzmann solver [7.14]. According to this calculation (Eqn. 7.2), the measured ratios (0.3 – 0.36) correspond to relatively high \( E/N \) in the range 160 - 290 Td! This is significantly higher than the values determined using other methods for similar conditions. For the 20 Torr, 10:33 O\(_2\):He conditions, analysis of terminal conditions (Sect. 6) resulted in an estimated \( E/N \) of 22-23 Td, while microwave interferometer measurements (Sect. 8) resulted in 16-21 Td.

### 7.3.3. Other Potential Methods of Optical \( E/N \) Measurement

The two optical methods for \( E/N \) measurements discussed above using O* or Ar* emissions ratios suffer from the same basic problem: the thresholds of the states being
compared are too close together, and therefore the method relies on the relative shape of the cross-section in order to correlate the line-ratio measurement to the $E/N$ (EEDF). While this approach benefits situations where the $E/N$ is significantly high (as in the case of Pagnon et al. [7.14] where the $E/N$ was approximately 100 Td), it does not apply well in ElectricOil discharges where the $E/N$ is lower (10-30 Td) and the relative pumping of various states becomes critically dependent on the cross-section shape near threshold (where the differences in cross-section are not well resolved). In other words, the pumping rates calculated at low $E/N$ for these species are not necessarily accurate, especially in a relative sense.

In order to produce an optical method with better sensitivity to $E/N$ it is necessary to compare states with significant separation in threshold. However, the thresholds of the states should not be too high, or the corresponding emission will be too weak, resulting in problems with signal to noise ratio. For balance of these two criteria, the energy gap between the thresholds of the two states should be on the order of the electron temperature [7.16]. The separation of the states in the O* method (Sect. 7.3.1) is 0.25 eV, and the separation in the Ar* method (Sect. 7.3.2) is 0.21 eV. While both the $I_{844}/I_{777}$ and $I_{751.5}/I_{750.4}$ ratio respond to the NO level, modeling this response properly based on the resolution of available cross-section data is difficult. However, the states used in TAA, O*(3p $^5P$) and Ar*(2p$_1$), have thresholds respectively of 10.74 and 13.48 eV, and this leads to the relative pumping rates having a strong $E/N$ dependence (see Fig. 4.17 in Sect. 4.4.4). Thus, if [O]/[Ar] is known by other means (for example O-NO recombination), it is possible to measure the relative intensity of O*(3p $^5P$) and Ar*(2p$_1$) and deduce the $E/N$. For typical conditions (10:33 O$_2$:He), applying TAA in a low power secondary discharge, and determining [O]/[Ar] from O-NO recombination method, the corresponding $E/N$ was approximately 22 Td.

However, this is not a practical method because it requires knowledge of the O-atom flow rate in the discharge, a parameter which varies significantly, and the whole reason for measuring $E/N$ is to obtain a calibration factor for TAA results! A more useful approach is to compare Ar*(2p$_1$) 750.4-nm to an emission with “large” threshold separation (a few eV), which also has a known (controllable) ground state.

One approach could be to compare emissions of Ar*(2p) with NIR emissions from trace amounts of neon, which are also in the range of the detectors applied in this study (the
PI-Acton/Apogee and Ocean Optics spectrometers). Some measurements of NIR emissions from a neon lamp measured with the Ocean Optics USB4000 spectrometer are given in Fig. 7.14, which plots the ratio of various neon lines to the Ne* emission at 724.5 normalized to the lowest current setting.

Figure 7.14. Measurements of Ne* emission ratios as a function of current in AC lamp using Ocean Optics USB4000 spectrometer. All emissions shown are relative to the line at 724.5 nm, normalized to the data point at the lowest current setting (13 mA). The wavelength, and upper state energy are given, and the energy separation of each upper state relative to the 724.5 nm emitting state at 18.38 eV is given in parentheses.

As the current in the lamp increases, the intensity of higher energy states relative to lower energy states increases. The change in the ratio increases as the separation between states increases; the ratio \( I_{717.4}/I_{724.5} \) increases by about 7% (0.194 eV separation), while the ratio \( I_{878.4}/I_{724.5} \) increases by 40% (1.756 eV separation). The relative intensities in Fig. 7.14 agree well with that obtained from a Boltzmann distribution with \( T_e \) in the range 0.395 – 0.420 eV (using parameters from [7.18]); an example is given in Fig. 7.15. If sufficient intensities of these states could produced without perturbing the O$_2$:He discharge dynamics significantly, a method of deducing the \( E/N \) optically by comparing Ne* emissions or both Ne* and Ar* emissions in NIR could be devised, since the pumping and of the various Ne* states in Fig. 7.14 (and others) are well-established (see for example [7.17]).
7.4. The NO(C→A) NIR Emission and NO(A,C→X) UV Emission

With the introduction of NO to the discharge, NO electronic excited states are pumped and emit in the NIR and UV. As discussed in Section 4.1.4, the NIR emission band of NO(C→A) at 1224 nm causes an experimental nuisance; because NO(C→A) emission is considerably more intense than the O2(a→X) emission at 1268 nm, it is difficult to make accurate measurements of O2(a→X) in order to determine the buildup of [O2(a)] within the discharge in the presence of NO [7.5]. The NO(A,C) states decay rapidly in comparison to O2(a) in the region downstream of the discharge, having short radiative lifetimes (10s of nanoseconds), and O2(a) measurements can be made downstream of the discharge. The level of NO(C) produced in the TCCRF discharge has an interesting behavior dependent on whether the discharge is normal or abnormal. The slope of NO(C) with power increases significantly at the normal-abnormal transition. This is demonstrated in Fig. 7.16, showing the peak intensity of NO(C→A) measured 5 cm downstream of a TCCRF discharge in a 1.6 cm I.D. tube with varied electrode length at (a) 30 Torr, and (b) 53 Torr.

![Figure 7.16. NO(C→A) emission as a function of RF power for varied transverse electrode length: (a) 30 Torr, (b) 53 Torr. The discharge tube was circular with a 1.6 cm I.D. and the flow mixture is 10:33:0.25 O2:He:NO. The measurements were made 5 cm downstream of the discharge exit. (N) denotes normal-mode discharge, and (A) denotes abnormal mode discharge.](image)

For both cases in Fig. 7.15, the normal mode operation was extended to higher RF power inputs by increasing the plate length. In results presented by Woodard et al. [7.19], increasing the electrode plate length from 25.4 cm showed significant improvements to O2(a) yield for similar conditions to Fig. 7.16. The NO(C→A) measurements indicate that the
abnormal discharge is drastically more efficient at pumping high energy states compared to the normal discharge. Most likely, this is due to increasing electron temperatures in the sheath region as voltage across the sheath increases in the abnormal case. This is the same reason why abnormal discharges tend to be inefficient for O$_2$(a) pumping (O$_2$(a) is at 0.98 eV compared to NO(C) at 6.47 eV).

Both NO(A) at 5.47 eV and NO(C) at 6.49 eV decay to the ground state, resulting in the emission of UV photons in the 190-340 nm range. Because the relative spontaneous emission rates of O$_2$(a) and NO(C) are known, it is possible to estimate [NO(C)], and determine both the amount of power carried in the flow by this species, and to estimate the power output of the associated UV photons from NO(A,C$\rightarrow$X). Assuming similar sensitivities of the spectrometer at 1224 and 1268 nm, the ratio of [NO(C)] to [O$_2$(a)] is proportional to the ratio of integral counts by

$$\frac{[NO(C)]}{[O_2(a)]} = \frac{A_{O_2(a-X)}}{A_{NO(C-A)}} \left( \frac{\int I_{NO(C\rightarrow A)} d\lambda}{\int I_{O_2(a\rightarrow X)} d\lambda} \right) = \frac{A_{O_2(a-X)}}{A_{NO(C-A)}} \left( \frac{\#NO(C \rightarrow A)\text{ counts}}{\#O_2(a \rightarrow X)\text{ counts}} \right) \quad (\text{Eqn. 7.3})$$

where $A_{O_2(a-X)} = 1/75 \text{ min} = 2.22 \times 10^{-4} \text{ s}^{-1}$ and $A_{NO(C-A)} = 1.34 \times 10^7 \text{ s}^{-1}$ [7.20], and $A_{O_2(a-X)}/A_{NO(C-A)} = 1.66 \times 10^{-11}$. As an example, in the case at 53 Torr and 1 kW RF with 25.4 cm electrodes (Fig. 7.15.b) the peak intensity of NO(C$\rightarrow$A) is approximately 33 times the peak intensity of O$_2$(a), such that (from Eqn. 7.3) $[NO(C)]/[O_2(a)] = 5.5 \times 10^{-10}$. The O$_2$(b) temperature at the measurement location was 600 K, and the O$_2$(a) yield measurement downstream was 12.5%, corresponding to $[O_2(a)] = 2.5 \times 10^{16} \text{ molec.-cm}^{-3}$, and $[NO(C)] = 1.4 \times 10^7 \text{ molec.-cm}^{-3}$. Thus, despite the high intensity of the NO(C$\rightarrow$A) emission (compared to O$_2$(a$\rightarrow$X) at 1268 nm), the density of the upper state of the emission is very small. Using the spontaneous emission rates for NO(C$\rightarrow$A) and NO(C$\rightarrow$X) ($A_{NO(C-X)} = 2.2 \times 10^7 \text{ s}^{-1}$) from Groth et al. [7.20], and assuming instantaneous emission of NO(A$\rightarrow$X), this corresponds respectively to volumetric emission rates of $1.82 \times 10^{14} \text{ photons-s}^{-1}\text{-cm}^{-3}$ in the NO(A$\rightarrow$X) band (5.45 eV), and $2.98 \times 10^{14} \text{ photons-s}^{-1}\text{-cm}^{-3}$ in the NO(C$\rightarrow$X) band (6.49 eV). Assuming a constant density of NO(C) throughout the discharge volume (51.3 cm$^3$), this corresponds to approximately 25 mW output in both bands. {Aside: For reference, the mercury UV emission at 253.7 nm which drives fluorescent light bulbs emits a 4.89 eV photon, with $A_{253.4} = 8.0 \times 10^6 \text{ s}^{-1}$ (NIST [7.18]), and a typical dose of Hg in Ar in fluorescent would be 10 mTorr in 300 mTorr}.  

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7.5. Conclusions about NO\textsubscript{X} Effects
From the data discussed above, the addition of NO to the O\textsubscript{2}:He discharge has some notable effects:

1) O\textsubscript{2}(a) production increases.

2) Quenchers are removed from the system (O, O\textsubscript{3}).

3) The shift in the ratio of atomic states suggests a shift in EEDF to lower electron temperature (lower $E/N$).

4) A source of UV photons is added in the form of electronically excited NO.

From examples given in Section 7.1, it is obvious that there is a gas kinetic effect which leads to either production or at least reduced quenching of O\textsubscript{2}(a), considering that O\textsubscript{2}(a) levels downstream of the discharge can be improved by either passing NO through the discharge or injecting it downstream. However, passing the NO through the discharge produces a larger effect. This effect is well described by the improved recombination of O-atoms to ground state O\textsubscript{2}, which both reduces gas-phase quenching of O\textsubscript{2}(a) by O-atoms and (as described by modeling in Section 2) promotes improved pumping of O\textsubscript{2}(a) within the discharge. In earlier work [7.2] the enhancement in O\textsubscript{2}(a) observed with the addition of NO\textsubscript{X} downstream of the discharge was thought to be from the reaction O + NO \rightarrow O\textsubscript{2}(X,a,b) + NO (k = 9.7\times10^{-12}) having a significant branching to O\textsubscript{2}(a); this mechanism was investigated by Azyazov et al. using UV photolysis of NO\textsubscript{2}, but no evidence of O\textsubscript{2}(a) production was found [7.3]. Based on this, the improved O\textsubscript{2}(a) observed when injecting NO\textsubscript{X} downstream of the discharge was due primarily to decreased quenching (improved lifetime) of O\textsubscript{2}(a) due to O-atom and ozone removal.

From measurements in Section 7.2, the introduction of NO\textsubscript{X} certainly leads to removal of both O-atoms and of O\textsubscript{3}. The O-atom production is reduced and the decay downstream of the discharge is increased. Because O-atoms are reduced, the buildup of O\textsubscript{3} is suppressed, and the level of O\textsubscript{3} downstream of the discharge was too low to measure when trace NO was introduced.

The measurements of atomic excited state ratios in Section 7.3 suggest that the addition of NO alters the EEDF to a lower electron temperature (a lower $E/N$). This is consistent with the decreasing terminal voltage measured as NO is added. However, in a few
examples with trace amounts of NO (given in Sections 6.2 and 7.1) the terminal voltage is unchanged while the O$_2$(a) production is significantly improved. In other words, the amount of NO required to maximize the improvement in O$_2$(a) yield has little impact on the terminal characteristics, and a small impact on $E/N$. It is perhaps questionable whether or not relative measurements of atomic emissions can be used as an indicator of the impact of NO on $E/N$. There does appear to be a correlation between Ar$^*(2p)$ line ratios and the electrical parameters, but the behaviors seen comparing Ar$^*(2p)$ line ratios and the O$^*(777$-nm)/O$^*(844$-nm) ratio results in some confusion. The O$^*$ line comparison is perhaps influenced by dissociative excitation, and therefore use of the Ar$^*$ line ratios or perhaps the line ratios of another trace noble gas such as neon [7.17] would be a better indicator. Some future work might involve investigating the influence of NO on the pumping of noble gas lines so that a more detailed model of pumping could be devised. Provided it can be assumed that NO has no significant impact on the pumping routes of Ar$^*$ lines, the end result of this work is that Ar$^*$ line ratios do indicate lower $E/N$ with NO added. The general problem with using the Ar$^*(2p)$ states is that the upper energy levels of these states are too close together in energy (12.9 – 13.5 eV). If emissions from states with larger energy spacing could be used, a better method of determining $E/N$ from excited atomic states could be devised.

Based on these experimental observations, and the behaviors seen in modeling with BLAZE [7.5], the beneficial improvement in O$_2$(a) observed when NO is added to the system is due to the contribution of three effects:

**Effect #1:** shifting of the average $E/N$ (or $T_e$) to conditions more optimal for O$_2$(a) production (original assumption, [7.1]),

**Effect #2:** improved electron-impact pumping of O$_2$(a) due to conversion of oxygen atoms to ground state O$_2$, and

**Effect #3:** reduced kinetic quenching of O$_2$(a) due to removal of oxygen atoms (and the associated buildup of ozone).

**Effects #1 and #2** would be much easier to establish if the 1268 nm emissions of O$_2$(a) could be measured within the discharge and directly compared with the BLAZE model. There would be an expectation of more rapid increase in 1268-nm emission with position along the discharge length when NO was added. However, this measurement is not possible due to strong NIR emissions near 1268 nm from NO excited states. It is obvious from data that the
addition of NO reduces the $E/N$ by lowered ionization potential. However, it has also been shown that the small amount of NO required to maximize the increase in $O_2(a)$ production has little impact on the terminal characteristics, suggesting little change in $E/N$. Based on modeling the well-established O-atom recombination mechanisms associated with NO and NO$_2$, Effect #2 is probably more important; Effect #2 is well established by both simple analytical modeling and modeling in BLAZE which show that $O_2(a)$ production efficiency is higher for lower ratios of $[O_2(a)]/[O_2(X)]$ due to the influence of super-elastic collisions (described in Section 2). This is perhaps the most important conclusion to be drawn from modeling of the discharge: the level of O$_2$ dissociation has influence on the $O_2(a)$ production because dissociation lowers the amount of ground state O$_2$ available for pumping. With increased $[O_2(a)]/[O_2(X)]$, the effective pumping rate of $O_2(a)$ (considering super-elastic effects) is slowed. This perhaps suggests that O$_2$ injection should be distributed along the discharge length, in order to reduce $[O_2(a)]/[O_2(X)]$, and improve overall $O_2(a)$ pumping efficiency.

Effect #3 is important both in the discharge (to reduce O-atom production), and downstream of the discharge to quench O-atoms and prevents ozone production through O-atom recombination. In ElectricOIL system development, it has been found that the NO flow rate can be adjusted to achieve the best output power conditions; this has to do with establishing the best O-atom flow rate which allows efficient dissociation of I$_2$, while also reducing $O_2(a)$ and I$^*$ quenching. In future work, active methods of I$_2$ dissociation will be applied (secondary injection discharges [7.21]), and NO$_X$ may be instrumental in removing O-atoms from the system prior to iodine injection in order to remove completely the influence of the $I^* + O \rightarrow I + O$ reaction and other quenching mechanisms which remove power carried in $O_2(a)$.

References


Important kinetic effects in the ElectricOIL system High Power Laser Ablation Conf. (Taos, NM, USA, 7-12 May 2006) Proc. SPIE 6261 6261R1

[7.3] Azyayov V N, Kabir M H, Antonov I O and Heaven M C 2007 Kinetics of O$_2$(a$^1\Delta_g$) and I($^{3}P_{1/2}$) in the Photochemistry of N$_2$O/I$_2$ Mixtures J. Phys. Chem. A 2007 111 6592-6599


8. Microwave Interferometer Measurements

While terminal characteristics of voltage and current can allow some insight into the plasma behavior, knowledge of electron density along with these terminal characteristics allows an improved understanding of the plasma conditions which is necessary for more accurately modeling the pumping of excited states in the ElectricOIL discharge. With this in mind, electron density measurements were made with a 4.1 GHz microwave interferometer (MWI) constructed about a TCCRF discharge with rectangular cross-section. Measurements were made for O₂/He/NO mixtures similar to those found in typical ElectricOIL discharges, and in air and pure helium. The interferometer frequency \( \omega \) was not well-suited for the plasma density regime, and results could only be obtained at relatively low discharge powers (compared to the full range of the RF source), where the plasma frequency \( \omega_p \) was lower than the microwave frequency. At higher powers, the microwave beam became highly attenuated due to the significant absorption and reflection characteristics of the plasma, and interpretation of the phase between the reference signal and signal passing through the plasma was not possible. The plasma density and collision frequency were determined by comparison of the complex attenuation measurements to a high-order model which allowed \( \nu_m \) and \( \omega_p \) to be similar in magnitude to \( \omega \), and took into account the reflections due to the plasma vessel walls.

8.1. Microwave Propagation in Plasma

Here the theory for a microwave beam propagating through a plasma will be derived, and the complex attenuation of the beam will be related to the plasma electron density \( n_e \) and the collision frequency \( \nu_m \) which is dependent on the plasma \( E/N \) (electric field-to-gas density ratio). The derivation is similar to those found in [8.1] or [8.2] and in the explanations given by Verdeyen [8.3], but allows for the collision frequency to be similar to the microwave frequency, and the attenuation per unit length to be significant compared to the phase shift per unit length. Using this model of wave propagation through the plasma, a modified theory which accounts for the influence of reflections at the air-quartz and quartz-plasma interfaces in the laboratory setup is applied.
8.1.1. Wave Equation for Microwave Propagation in Plasma with Collisions

The propagation of the microwaves though the plasma is described by Maxwell’s equations, shown here in SI units:

\[ \varepsilon_0 \nabla \cdot \mathbf{E} = \rho \]  \hspace{1cm} (Eqn. 8.1.a)

\[ \mu_0 \nabla \cdot \mathbf{H} = 0 \]  \hspace{1cm} (Eqn. 8.1.b)

\[ \nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t} \]  \hspace{1cm} (Eqn. 8.1.c)

\[ \nabla \times \mathbf{H} = \mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \]  \hspace{1cm} (Eqn. 8.1.d)

Assuming a homogeneous, linear, isotropic medium, Ohm’s law gives the conductivity \( \sigma \) which relates the current density \( \mathbf{J} \) to the electric field intensity \( \mathbf{E} \),

\[ \mathbf{J} = \sigma \mathbf{E} \]  \hspace{1cm} (Eqn. 8.2)

Taking the curl of Eqn. 8.1.c and substitution of Eqn. 8.1.d gives

\[ -\nabla \times (\nabla \times \mathbf{E}) = \mu_0 \left[ \frac{\partial \mathbf{J}}{\partial t} + \varepsilon_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} \right]. \]  \hspace{1cm} (Eqn. 8.3)

Introducing the vector identity \( \nabla \times (\nabla \times \mathbf{E}) = \nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} \) into Eqn. 8.3 results in the wave equation

\[ \nabla^2 \mathbf{E} - \nabla \frac{\rho}{\varepsilon_0} - \mu_0 \frac{\partial \mathbf{J}}{\partial t} = \mu_0 \varepsilon_0 \frac{\partial^2 \mathbf{E}}{\partial t^2}. \]  \hspace{1cm} (Eqn. 8.4)

The second term on the L.H.S. of Eqn. 8.4 can be eliminated by considering the charge continuity equation,

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0 \]  \hspace{1cm} (Eqn. 8.5)

If the assumption of plane waves is made, there is no variation in current along the direction of propagation, and therefore the second term in Eqn. 8.5 is zero, and the charge density must be constant with time, and with the assumption of charge neutrality in the plasma (\( n_e = n_i \)), \( \rho = \text{constant} = 0 \). Assuming waves with the time dependence \( \exp(j \omega t) \), and using Eqn. 8.2

\[ \frac{\partial \mathbf{J}}{\partial t} = j \omega \sigma \mathbf{E} \]  \hspace{1cm} (Eqn. 8.6)

Substitution of \( c = (\mu_0 \varepsilon_0)^{-1/2} \) and Eqn. 8.6 into Eqn. 8.4 results in
\[ \nabla^2 \mathbf{E} - \frac{1}{c^2} \frac{\sigma_c}{\varepsilon_0} j\omega \mathbf{E} = \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2}. \]  
(Eqn. 8.7)

For propagation along the x-direction only, with the electric field vector in the y-direction, the 1-dimensional wave equation becomes

\[ \frac{\partial^2 E_y}{\partial x^2} - \frac{1}{c^2} \frac{\sigma_c}{\varepsilon_0} j\omega E_y = \frac{1}{c^2} \frac{\partial^2 E_y}{\partial t^2}. \]  
(Eqn. 8.8)

8.1.2. The Complex Plasma Conductivity

The complex conductivity of the plasma \( \sigma_c \) can be determined using the velocity equation for the average electron

\[ m_e \frac{d\mathbf{w}}{dt} + m_e v_m \mathbf{w} = e \mathbf{E}. \]  
(Eqn. 8.9)

Here, the second term is the directed momentum loss per second due to electron-molecule collisions, and \( v_m \) is the electron-molecule collision frequency. Assuming the time dependence \( \exp(j\omega t) \), Eqn. 8.9 becomes

\[ \mathbf{w} = \frac{e \mathbf{E}}{m_e \left[ v_m + j\omega \right]}. \]  
(Eqn. 8.9)

Rewriting Eqn. 8.2, the current density becomes

\[ \mathbf{J} = \sigma_c \mathbf{E} = n_e \mathbf{w} = \frac{n_e^2 \mathbf{E}}{m_e \left[ v_m + j\omega \right]}. \]  
(Eqn. 8.10)

From this, the complex conductivity is

\[ \sigma_c = \sigma_R + j\sigma_I = \frac{n_e^2 \mathbf{E}}{m_e \left[ v_m^2 + \omega^2 \right]} \left( v_m - j\omega \right) = \omega_p^2 \varepsilon_0 \frac{v_m - j\omega}{v_m^2 + \omega^2}. \]  
(Eqn. 8.11)

where \( \omega_p \) is the plasma frequency.

8.1.3. The Complex Propagation Constant

The complex propagation constant is defined by

\[ \tilde{\gamma} = \alpha + j\beta, \]  
(Eqn. 8.12)
where $\alpha$ is the attenuation coefficient (in nepers/meter) and $\beta$ is the phase coefficient (in radians/meter).

Assuming waves of the form

$$E_y = E_0 \exp(j \omega t - \tilde{\gamma} x) \quad \text{(Eqn. 8.13)}$$

and substitution of Eqn. 8.11 into Eqn. 8.8 results in

$$\tilde{\gamma}^2 = (\alpha + j \beta)^2 = \alpha^2 - \beta^2 + j 2 \alpha \beta$$

$$= -\frac{\omega^2}{c^2} \left[ \frac{\omega_p^2}{v_m^2 + \omega^2} \right] + j \frac{\omega^2}{c^2} \frac{\omega_p^2}{v_m^2 + \omega^2} \left( \frac{v_m}{\omega} \right) \quad \text{(Eqn. 8.14)}$$

$$= -\beta_0^2 \left[ \frac{1}{1 + S^2} - j \left( \frac{NS}{1 + S^2} \right) \right]$$

where the parameters $\beta_0 = \frac{\omega}{c}$, $N = \left( \frac{\omega_p}{\omega} \right)^2$, and $S = \frac{v_m}{\omega}$ have been introduced for simplification. The notations for normalized electron density $N$ and normalized collision frequency $S$ are taken from Bachynski and Graf [8.4]. Equation 8.14 is satisfied if $\alpha$ and $\beta$ are

$$\alpha = \beta_0 \left[ \frac{K - K_R}{2} \right]^{1/2}, \quad \text{and} \quad \text{(Eqn. 8.15)}$$

$$\beta = \beta_0 \left[ \frac{K + K_R}{2} \right]^{1/2}, \quad \text{(Eqn. 8.16)}$$

where $\tilde{K} = -\left( \frac{\tilde{\gamma}}{\beta_0} \right)^2$ is the complex dielectric constant, and $K_R$ is the real part of $\tilde{K}$. Eqns. 8.15 and 8.16 combined with Eqn. 8.14 determine the complex attenuation coefficient $\tilde{\gamma}$ as a function of the normalized plasma parameters $N$ and $S$.

### 8.1.4. Modified Theory Accounting for Reflections and Walls

A modified theory is described here which accounts for reflections at interfaces between mediums, and propagation though the quartz walls of the discharge vessel. The
result of this modified theory is an equation that describes the overall transmission coefficient as a function of the normalized plasma parameters $N$ and $S$ and plasma vessel dimensions (length of propagation through plasma $\ell$ and wall thickness $d$). The laboratory setup can be modeled as sketched in Fig. 8.1.

Figure 8.1. Sketch of plasma vessel and microwave interferometer “horns” setup. Microwaves propagate along the x-axis between the waveguide adapters (plane waves assumed in analysis). The microwave electric field is in the y-direction, while the magnetic field is along the z-axis. Microwaves propagate through five regions: (0 and 4) air, (1 and 3) quartz and (2) plasma.

The waves are considered to be plane waves. To determine the reflections, the wave impedance in each medium must be determined. In air, it is assumed to be that of free space, in the quartz it is determined assuming a dielectric constant of 3.75, and in the plasma it is determined by the plasma parameters in Section 8.1.3.

The electric and magnetic fields can be expressed as

\[
\begin{align*}
\mathbf{E} & = E_0 \exp(j \omega t) \exp(-\gamma \cdot \mathbf{r}), \\
\mathbf{H} & = H_0 \exp(j \omega t) \exp(-\gamma \cdot \mathbf{r}),
\end{align*}
\]  

(Eqn. 8.17)

with the definitions $\gamma = \gamma_x \mathbf{a}_x + \gamma_y \mathbf{a}_y + \gamma_z \mathbf{a}_z$ and $\mathbf{r} = r_x \mathbf{a}_x + r_y \mathbf{a}_y + r_z \mathbf{a}_z$. For propagation through the plasma, Substitution of Eqn. 8.17 into Eqns. 8.1.c and d gives
\[-\gamma \times \mathbf{E}_0 = -j\omega\mu_0\mathbf{H}_0 \quad \text{(Eqn. 8.18)}\]
\[-\gamma \times \mathbf{H}_0 = (\sigma_c + j\omega\varepsilon_0)\mathbf{E}_0 \quad \text{(Eqn. 8.19)}\]

For plane wave propagation in the x-direction (\(\mathbf{E}\) in the y-direction, and \(\mathbf{H}\) in the z-direction), the wave impedance in the plasma becomes

\[\eta_p = \frac{E_0}{H_0} = \frac{j\omega\mu_0}{\gamma} = \frac{\gamma}{(\sigma_c + j\omega\varepsilon_0)} \quad \text{(Eqn. 8.20)}\]

From the wave equation solution in Section 8.1.1, \(\gamma^2 = j\omega\mu_0(\sigma_c + j\omega\varepsilon_0)\), which results in

\[\eta_p = \frac{E_0}{H_0} = \left(\frac{\mu_0}{\varepsilon_0} \left(1 - j\frac{\sigma_c}{\omega\varepsilon_0}\right)^{-1/2}\right) = \eta_0\left(1 - j\frac{\sigma_c}{\omega\varepsilon_0}\right)^{-1/2} = \eta_0(K^{1/2}) \quad \text{(Eqn. 8.21)}\]

Here, \(\eta_0 = (\mu_0/\varepsilon_0)^{1/2} = 377 \, \Omega\) is the wave impedance of free space, considered the value of the wave impedance in the air and the no plasma case (\(\sigma_c = 0\)). For the propagation through the quartz wall, the Maxwell’s equations must be set up to include the polarization and magnetization of the quartz. A similar derivation to Eqns. 8.17-21 shows the wave impedance in quartz to be

\[\eta_q = \frac{E_0}{H_0} = \eta_0\left(\frac{\mu_q}{\varepsilon_q}\right)^{1/2}, \quad \text{(Eqn. 8.22)}\]

where \(\mu_q = 1\) and \(\varepsilon_q = 3.75\) are the relative permeability and permittivity of the quartz.

\begin{center}
\begin{tabular}{c|c|c}
\textbf{Interface} & 
\textbf{Medium A} & 
\textbf{Medium B} \\
\hline
& \(\eta_A\) & \(\eta_B\) \\
\hline
& \(\mathbf{E}_A^+\) & \(\mathbf{E}_B^+\) \\
& \(\mathbf{H}_A^+\) & \(\mathbf{H}_B^+\) \\
& \(-\gamma_A \mathbf{a}_x\) & \(-\gamma_B \mathbf{a}_x\) \\
\hline
& \(\mathbf{E}_A^-\) & \(\mathbf{E}_B^-\) \\
& \(\mathbf{H}_A^-\) & \(\mathbf{H}_B^-\) \\
& \(-\gamma_A \mathbf{a}_x\) & \(-\gamma_B \mathbf{a}_x\) \\
\end{tabular}
\end{center}

\begin{center}
\textbf{Matching equations:}
\end{center}

\[E_A^+ + E_A^- = E_B^+ + E_B^- \quad \text{(Eqn. 8.23)}\]
\[H_A^+ - H_A^- = H_B^+ - H_B^- \quad \text{and} \quad \frac{E_A^+}{\eta_A} - \frac{E_A^-}{\eta_A} = \frac{E_B^+}{\eta_B} - \frac{E_B^-}{\eta_B} \quad \text{(Eqn. 8.24)}\]

Figure 8.2. Boundary condition matching between two mediums.
In order to determine the overall complex transmission coefficient of the electric field, the incident and reflected electric and magnetic fields are summed at each interface. This is illustrated in Figure 8.2, where the superscript denotes the direction of propagation, “+” for right-running, and “−” for left-running. The goal is to relate the transmitted wave $E_{4+}$ to the incident wave $E_{0+}$. This is done by applying Eqns. 8.23 and 8.24 at each interface from right to left, accounting for the propagation of right-running and left-running waves through each medium. After a considerable amount of algebra, the solutions for the overall transmission and reflection coefficients of the plasma vessel are determined to be (as given by [8.4])

$$T = \frac{E_{4+}}{E_{0+}} = \frac{1}{2} \left[ \left( \frac{n_d}{n_q} \right)^2 + \left( \frac{n_p}{n_q} \right)^2 \sinh^2 \gamma' d \sinh \delta \right]$$

$$R = \frac{E_{0−}}{E_{0+}} = T \left[ \left( \frac{n_d}{n_q} \right)^2 + \left( \frac{n_p}{n_q} \right)^2 \sinh^2 \gamma' d \sinh \delta \right]$$

In Eqns. 8.25 and 8.26, $\gamma'$ denotes the attenuation through the quartz. For the case in which $n_p = n_d$ and the quartz walls are neglected, the above reduces to $T = \exp(-\gamma \ell)$ and $R = 0$. Equation 8.25 can be used to determine the attenuation and the phase shift of the microwave beam as it passes through the plasma vessel. The interferometer setup was used to measure the change in attenuation (in dB) due to the plasma given by

$$\Delta T = -20 \log_{10} \left( \frac{T}{T_0} \right),$$

(Eqn. 8.27)

where $T_0$ is the (complex) transmission coefficient in the zero plasma case. The change in phase shift due to the plasma was determined by
\[ \Delta \phi = \phi - \phi_0, \quad \text{(Eqn. 8.28)} \]

where the subscript “0” again refers to the zero plasma case. The phase shift (in degrees) through the vessel in either case was determined by

\[ \phi = \frac{180}{\pi} \arctan \left( \frac{\text{Im}(T)}{\text{Re}(T)} \right). \quad \text{(Eqn. 8.29)} \]

This assumes \(-90^\circ < \phi < 90^\circ\) (in the no plasma case, the total phase shift was slightly less than 360°, and since experimental phase shifts due to the plasma were significantly less than 90° in magnitude, Eqn. 8.29 was sufficient). In addition to the attenuation and phase, it is also useful to know the reflected and absorbed power fractions given respectively by

\[ P_{\text{refl}} = R \bar{R}, \text{ and } \]
\[ P_{\text{abs}} = 1 - R \bar{R} - T \bar{T}. \quad \text{(Eqn. 8.31)} \]

Since \(\Delta T\) and \(\Delta \phi\) were the values determined in the interferometer experiment, Eqns. 8.25 and 8.26 were used implicitly to determine the normalized plasma parameters \(N\) and \(S\). Figure 8.3 shows the (a) attenuation, (b) phase shift, (c) absorbed power, and (d) reflected power as a function of normalized electron density \(N\) for varied normalized collision frequency \(S\) determined using Eqns. 8.25-31.

The attenuation (Fig. 8.3.a) increases significantly with electron density over the range shown and its dependence on collision frequency over the range is fairly complex. At low \(N\) and low \(S\) there is a regime in which the microwave transmission increases due to the plasma (see for example \(S = 0.1, N < 0.4\)). For higher \(S\), attenuation is strictly increasing with \(N\), with the slope having a strong dependence on \(S\). The phase shift (Fig. 8.3.b) is strictly increasing with \(N\), but decreases with \(S\).

Figure 8.3.c shows that the fraction of power absorbed by the plasma \(P_{\text{abs}}\) is significant, with a strong dependence on both \(N\) and \(S\). As seen in Figure 8.3.d the reflected power fraction \(P_{\text{refl}}\) is significant for zero electron density (no plasma, \(N = 0\)); as \(N\) increases, the reflected power initially decreases, reaches a minimum dependent on \(S\), and then increases. For high electron densities, where attenuation is high (low transmitted power), the exchange between absorbed and reflected power with varied \(S\) is obvious. For example, for \(N = 1\), the absorbed power reaches a maximum \((P_{\text{abs}} \sim 0.9)\), while the reflected power reaches...
a minimum ($P_{\text{refl}} \sim 0.07$) at $S \sim 1$. At $(N, S) = (1, 0.1)$, however, the relative fractions of transmitted, reflected, and absorbed power are 0.05, 0.6, and 0.35 respectively.

Figure 8.3. Calculated attenuation, phase shift, absorbed power, and reflected power as a function of normalized electron density $N$ for varied normalized collision frequency $S$. The microwave frequency is 4.083 GHz, the separation between the vessel walls is 6.0 cm, and the quartz wall thickness is 0.3 cm.

The microwave source used in the experiment operated at 4.083 GHz; therefore $N = 1$ ($\omega^2 = \omega_p^2$) corresponds to an electron density of $2.07 \times 10^{11}$ cm$^{-3}$, and $S = 1$ corresponds to an effective collision frequency of $2.57 \times 10^{10}$ s$^{-1}$. For the moderate pressure RF plasmas investigated in ElectricOIL work (few – 100 Torr), the electron densities are expected to be
in the range of $1 \times 10^9$ – $1 \times 10^{11}$ cm$^{-3}$, while the collision frequency is expected to be roughly $\sim 3 \times 10^9$ s$^{-1}$ per Torr (based on estimates from [8.5, 8.6]). Therefore, the ranges of $N$ and $S$ in Fig. 8.3 should be similar to those expected for ElectricOIL discharges.

### 8.2. Microwave Interferometer Setup, Procedures, and Data Reduction

#### 8.2.1. MWI Setup

The MWI setup consisted of the following:

1. A General Radio type 1360-A Microwave Oscillator operating at $\sim$4.08 GHz.
2. A FXR model N414A wave meter to measure the microwave frequency.
3. A Narda model 3043-10 coaxial directional coupler to split the source signal into the plasma and reference signals.
4. A Sperry model D44S5 Isolator to isolate the source from reflected signals.
5. 2 HP G281A waveguide adapters (G-band, WR-187) which serve as horns positioned about the plasma vessel.
6. A phase shifter device to change the relative length of the interferometer arms; two phase shifters were used: a Narda model 3753B, and a General Radio Trombone.
7. A series of step attenuators to attenuate the signal in the reference arm of the interferometer. HP 8494B 1-dB step and HP 8495B 10-dB step attenuators were used.
8. A Narda Microline model 3034 coaxial hybrid which adds together the plasma arm and reference arm signals.
9. 2 HP 423B crystal detectors which monitor the hybrid outputs.
10. A Tektronix TDS 2024 oscilloscope to read the crystal detectors.

A typical setup is sketched in Fig. 8.4.
8.2.2. MWI Procedure

The goal of the experiment was to measure the attenuation and phase shift of the microwave beam as it passes through the plasma region. This was done by summing the reference and plasma arm signals with the coaxial hybrid and measuring the result. The two signals, the one which passed through the plasma vessel $E_p$ and the one which passed though the reference arm $E_r$ can be represented using a phasor diagram, as in Fig. 8.5. The measurements made at the hybrid bridge correspond to the vector difference $E_{B1}$ and sum $E_{B2}$ of the two phasors.

Figure 8.4. A typical MWI setup for measurements in a TCCRF discharge.

Figure 8.5. Phasor diagram of MWI signals. The difference $E_{B1}$ and sum $E_{B2}$ of the reference arm and plasma arm signals are measured at the hybrid coaxial coupler outputs.
The procedure used in measurements was as follows:

1. With plasma off, balance the reference attenuation and phase shifter to obtain a “null” (zero voltage at the difference detector) which corresponds to the signals passing though the plasma arm and reference arm and reaching the detector through the hybrid being 180° out of phase and of equal amplitude.

2. Turn on the plasma, and establish a minimum signal at the difference detector by adjusting the phase shifter.

3. Use the change in phase shifter setting, and the magnitude of the signal to determine the change in phase shift and the attenuation through the plasma arm.

### 8.2.3. Determining the Voltage Response of the Detectors

The voltage measurement from the HP 423B detectors is a function of the electric field amplitude of the hybrid signal. In order to determine the electric field amplitude attenuation, the voltage response to the field must be known. This was determined by measuring the voltage response as the source signal power \( P \sim E^2 \) through the reference arm was discretely varied by changing the setting of an attenuator placed between the source and detector. The bridge voltage was found to depend on the bridge electric field amplitude with the form

\[
V_B = A \left( E_B^2 \right)^C .
\]

(Eqn. 8.32)

The value of \( C \approx 0.59 \) was determined. The proportionality constant \( A \) is not known, but is unnecessary since the attenuation in the electric field amplitude and not the actual magnitude is required in the data analysis. Therefore, \( A = 1 \) was assumed in calculations.

### 8.2.4. Determining the Attenuation and Phase Shift

The model in Section 8.1.4 was used to relate experimental measurements of attenuation and phase shift to the normalized plasma parameters \( N \) and \( S \). The shift in phase angle due to the plasma was determined by

\[
\Delta \phi = \phi_{p,\text{min}} - \phi_{0,\text{null}} ,
\]

(Eqn. 8.33)

the difference between the phase shifter setting for a minimum with plasma, and the setting for a null without plasma. To determine the attenuation due to the plasma, it was necessary
to determine the magnitude of the hybrid bridge signal relative to the reference arm signal. After the null was set with plasma off, the plasma and reference signals had the same magnitude (denoted $|T_0|E_0$), but were summed together 180° out of phase to give zero voltage at the (difference) detector. The plasma was ignited, and the phase shift was set to minimize the bridge detector voltage. In this case, the plasma arm signal and reference arm signal are 180° out of phase, but the magnitudes are not equal and the reference signal is larger such that

$$E_{b1} = E_R - E_P.$$

(Eqn. 8.34)

$E_P$ is the magnitude of the signal through the plasma, $E_R$ is the reference signal magnitude, and $E_{b1}$ is the hybrid bridge (difference) signal magnitude. The change in attenuation due to the plasma can then be determined from

$$
\frac{|T|}{|T_0|} = \frac{E_P/E_0}{E_R/E_0} = 1 - \frac{E_B}{E_R}.
$$

(Eqn. 8.35)

In order to use Eqn 8.35, $E_R$ must be determined by some means. This was accomplished by first setting a null with the plasma off, and then monitoring the hybrid (difference channel) voltage as the phase shifter setting was varied. In this case $E_P = E_R$ and the hybrid bridge voltage was related to the signal magnitude by

$$V_B = \left(2E_R^2\left(1 - \cos(\Delta\phi)\right)\right)^C
$$

(Eqn. 8.36)

and $E_R$ was readily determined from a best fit to the data.

8.3. MWI Measurements and Analysis

MWI measurements were taken as a function of RF power for varied mixture and pressure. The electron density and collision frequency results obtained using phase shift and attenuation measurements from MWI in conjunction with the model described in Section 8.1 are shown in Figure 8.6.
Figure 8.6. MWI measurements for a variety of flow conditions as a function of RF power input: (a) electron density, (b) collision frequency.

The data shown in Fig. 8.6 correspond to abnormal discharge conditions meaning that the current density and voltage both increase as RF input increases, and that the plasma fills the entire discharge volume (457 cm³). As a result, the measured electron density increased with RF input power. Figure 8.7 shows the calculated collision frequency determined by the Blaze model Boltzmann solver [8.7] for the mixtures used in experiment (Fig 8.6). For the 10:33 O₂:He mixture, the measured collision frequencies are similar to the calculation in the range of 2-20 Td (1 Td = 1x10⁻¹⁷ V·cm²); the measurements in helium are considerably higher than the modeling result (over the entire range shown), while measurements in air correspond to modeling result at high $E/N (> 50$ Td).
Figure 8.7. Collision frequency calculated using the Blaze Model Boltzmann solver for the various mixtures used in experiment. The addition of trace NO to the 10:33 O₂:He case changes the result by less than a percent.

Figure 8.8. Plasma $E/N$ calculated using Eqn. 8.42 and data in Fig. 8.6. The temperature is assumed to be 300 K in the helium case, and is deduced from $O_2(b)$ measurements in the cases with oxygen.

Using the results in Fig. 8.6, it is possible to define the DC conductivity for the plasma and given that the power depositions in the plasma can be estimated from the RF power input, this allows estimation of the electric field and therefore the plasma $E/N$ if the temperature is known. The RF plasma conductivity can be defined as

$$\sigma_{RF} = \frac{\varepsilon_0 \omega_p^2}{V_m + j \omega_{RF}}$$

(Eqn. 8.37)

Because $\omega_{RF} \ll \nu_m$, the RF conductivity can be treated as a DC conductivity defined as

$$\sigma_{DC} = \frac{\varepsilon_0 \omega_p^2}{V_m} = \frac{n_e e^2}{m_e V_m}.$$  

(Eqn. 8.38)

The time-average RF power per unit volume absorbed by the plasma is given by

$$P_{abs} = \frac{1}{\tau} \int_0^\tau \mathbf{J}_T(t) \cdot \mathbf{E}(t) \, dt = \frac{1}{2} \text{Re}(\mathbf{J}_T \cdot \mathbf{E}^*) = \frac{1}{2} \text{Re}(\mathbf{\tilde{J}}_T \cdot \mathbf{\tilde{E}})$$

(Eqn. 8.39)

Where $\mathbf{\tilde{J}}_T$ and $\mathbf{\tilde{E}}$ are amplitudes assumed to be spatially uniform (for example $\mathbf{E}(t) = \text{Re}(\tilde{\mathbf{E}} e^{j \omega_{RF} t})$). The total current density (conduction and displacement) is related to the electric field by

$$\mathbf{\tilde{J}}_T = (\sigma_{RF} + j \omega_{RF} \varepsilon_0) \mathbf{\tilde{E}}$$

(Eqn. 8.40)
Using Eqn. 8.40 to substitute for either $\tilde{J}_T$ or $\tilde{E}$ in Eqn. 8.39 results in definition of the collisional (ohmic) absorbed power in terms of either the electric field amplitude or the current density amplitude as

$$P_{\text{ohm}} = \frac{1}{2} |\tilde{E}|^2 \sigma_{\text{DC}} = \frac{1}{2} |\tilde{J}_T|^2 \frac{1}{\sigma_{\text{DC}}} \quad \text{(Eqn. 8.41)}$$

From this, the electric field-to-gas density ratio in the plasma can be defined as

$$\frac{E_{\text{RMS}}}{N_g} = \frac{1}{N_g} \sqrt{\frac{P_{\text{ohm}}}{\sigma_{\text{DC}}}}, \quad \text{(Eqn. 8.42)}$$

where $E_{\text{RMS}} = |\tilde{E}|/\sqrt{2}$. For the cases with oxygen, the dependence of the gas temperature as a function of power and pressure is well known from spectral measurements of O$_2$(b) at 762 nm, allowing determination of gas density $N_g$.

A calculation of $E/N$ using Eqn. 8.42 and the data in Fig. 8.6 along with O$_2$(b) temperature data from other experiments (for example actinometry data taken in the same discharge configuration) is shown in Fig. 8.8. The scatter in the results is significant, and there is no clear trend with RF input or NO. The $E/N$ results for the 10:33 O$_2$:He cases (with and without NO) are in the range 20-34 Td (1 Td = 1x10$^{-17}$ V-cm$^2$) for 5 Torr cases and 16-21 Td for the 20 Torr cases, while the results with pure helium are ~8 Td (assuming $T = 300$ K to determine the density).

The current density $J_{T,\text{RMS}} = |\tilde{J}_T|/\sqrt{2}$ calculated using Eqn. 8.41 is plotted in Fig. 8.9. As expected for these abnormal cases from terminal measurements in the 20 Torr cases, the current density rises linearly with the RF power input. The plasma voltage determined from MWI data is compared to the terminal voltage (using a HV probe and Pearson current probe) in Fig. 8.10.
8.4. Discussion and Suggested Future Work

The MWI results described here are of interest for comparisons to the computational model of the ElectricOIL discharge. However, the plasma frequency and the collision frequency were similar to or greater than the microwave frequency which led to large attenuation and small phase shifts, and therefore the accuracy of the results was not as good as desired. The agreement in trends between the data and analytical model is somewhat encouraging and at least establishes that a more adequate MWI setup could be devised which is better suited for the ElectricOIL plasma conditions.

The \( \frac{E}{N} \) deduced from MWI measurements of conductivity was similar to the expected range based on analysis of terminal characteristics for the 10:33 O\(_2\):He mixture; the results could be consistent with the less-than-optimal O\(_2\)(a) production efficiency observed for the 20 Torr conditions. The 10:33:0.15 O\(_2\):He:NO, 20 Torr case corresponds to ~12.5% O\(_2\)(a) yield at 800 W, and the efficiency of O\(_2\)(a) production decreases with power for the abnormal discharge. The modeling shows that the efficiency of production decreases sharply as O\(_2\)(a) is produced for constant \( \frac{E}{N} \), and indicates that the \( \frac{E}{N} \) must increase as O\(_2\)(a) is produced in order to attain the highest yields (see Section 2.3).

Comparison of the calculated current density and plasma voltage at 20 Torr with terminal characteristics from Section 7 provides an interesting result (Fig. 8.10). Although
the current density determined from MWI rises linearly with RF power similar to the linear rise in terminal current with power, the voltage determined from MWI is significantly lower than, and remains relatively constant compared to the terminal (electrode) voltage which increases linearly with RF power input (and current). This indicates that the capacitive sheaths (and quartz wall) must be sustaining the increasing voltage drop as the RF power increases in the abnormal case, while the bulk plasma maintains a voltage drop corresponding to a relatively constant $E/N$. If the current density in the sheath is primarily displacement current, the increasing current density would eventually lead to a breakdown of the $\alpha$-mode sheath, and a transition from homogeneous to inhomogeneous conditions as discussed in Section 7.

Two main problems with the MWI system used in the experiments described here are (1) the microwave frequency is too low compared to the characteristic frequencies of the plasma, and (2) the physical dimensions of the waveguide used are too large to offer spatial resolution of measurements. Fortunately, these two issues suggest the same thing, designing an interferometer at higher frequency such that $\omega >> \omega_p$. Using a microwave frequency which is significantly larger than the plasma and collision frequencies should allow less attenuation, and therefore reduce the “cutoff”-like behaviors observed in the experiments discussed here (at high RF powers). Also, the size of the microwave waveguides and horns can be reduced with higher frequency, allowing the possibility of a smaller microwave beam which can be translated along the length of the transverse plasma to obtain adequate spatial measurements, and perhaps be applied to a transverse configuration with a smaller gap.

The effects of refractive defocusing on validity of the attenuation measurement must also be considered. For the setup used in this investigation, the microwaves are not well guided through the plasma as there is no boundary perpendicular to the z-direction (flow direction) in the plasma region. This leads to waves which do not propagate perpendicular to the flow direction axis (z-axis) being refracted away from the axis running between the antennas (x-axis), which influences the attenuation in a complex fashion dependent on changes in refractive index at interfaces, gradients in the plasma, and the changes in the plasma as RF power changes. This issue could perhaps be overcome by construction of a transverse RF discharge within a waveguide which allows propagation of the microwave frequency, as is discussed in [8.2, pg. 163], or by applying a technique similar to that used by
Raicu in helium discharge at low pressure [8.8]. This type of discharge would not be practical in terms of laser development, but might be an adequate system for testing the ability of the Blaze model to match the plasma characteristics of ElectricOIL discharges. An alternative approach is to use a configuration in which the effects of refractive defocusing can be appropriately modeled (see for example Bachynski [8.9]).

References


[8.3] Verdeyen J T 2009 Personal communication and hand written notes


9. The Progress in ElectricOIL Gain and Power Extraction

This section will overview the improvements in ElectricOIL gain and power output between 2004 and late 2008. First, a heuristic model of laser power extraction will be discussed. Then the systematic improvements in gain and laser power will be summarized, reviewing results obtained with various configurations. Gain measurements in various configurations will then be compared to BLAZE modeling. After this, some issues related to power extraction observed in recent experiments (gain recovery measurements and optical losses) will be discussed. A discussion of overall laser system performance will conclude the section.

9.1. A Heuristic Model of Laser Power Output

The efficiency of power output from an oxygen-iodine laser can be modeled with a heuristic equation that is a function of \( \text{O}_2(\text{a}) \) yield, cavity temperature, and component efficiencies. Hon et al. defines the \textbf{chemical efficiency} of a COIL device as

\[
\eta_{\text{chem}} = \frac{P_{\text{out}}}{\dot{n}_{\text{Cl}} \cdot E_{I^*}} = U_{\text{Cl}} \cdot (Y - Y_{\text{OT}}(T) - Y_{\text{loss}}) \cdot \eta_{\text{sys}},
\]  
(Eqn. 9.1)

where \( \dot{n}_{\text{Cl}} \) is the input flow rate of chlorine in mmol/s, \( E_{I^*} \) is the energy in joules per millimole of \( I^* \), \( U_{\text{Cl}} \) is the chlorine utilization which is the fractional conversion of chlorine to oxygen in the singlet-oxygen generator (SOG) and \( Y \) is the fractional \( \text{O}_2(\text{a}) \) yield defined by \([\text{O}_2(\text{a})]/(\text{[O}_2(\text{a})]+[\text{O}_2(\text{X})]) \) [9.1]. \( Y_{\text{OT}} \) is the \( \text{O}_2(\text{a}) \) yield for optical transparency as defined in Section 2, \( Y_{\text{loss}} \) is the \( \text{O}_2(\text{a}) \) yield lost due to quenching and \( \text{I}_2 \) dissociation between the \( \text{O}_2(\text{a}) \) generator and resonator, and \( \eta_{\text{sys}} \) is an overall system efficiency representing the product of mixing, geometric, residence time, and optical extraction efficiencies [9.1]. A similar parameter, the \textbf{electrical efficiency} can be defined for ElectricOIL,

\[
\eta_{\text{elec}} = \frac{P_{\text{out}}}{RF_{\text{sys}}} = \left( \frac{\dot{n}_{\text{O}_2} \cdot E_{I^*}}{RF_{\text{sys}}} \right) \cdot (Y - Y_{\text{OT}}(T) - Y_{\text{loss}}) \cdot \eta_{\text{sys}},
\]  
(Eqn. 9.2)

In Eqn. 9.2, \( RF_{\text{sys}} \) is the radio-frequency discharge power input in watts, \( \dot{n}_{\text{O}_2} \) is the input flow rate of oxygen in mmol/s, and all other parameters are as in Eqn. 9.1. In using \( E_{I^*} \) as the characteristic energy in both Eqn. 9.1 and 9.2, the exothermic loss in the pumping reaction is accounted for \((E_{I^*}/E_{\text{O}_2(a)} = 0.965)\). The dependence of output power on system parameters...
can be determined based on these simple heuristic equations. For set values of \( O_2(a) \) yield, cavity temperature, and efficiencies (system and chemical or electrical), the COIL device output will be proportional to chlorine flow rate, and the ElectricOIL device power output will be proportional to oxygen flow rate. In both systems, to obtain high efficiency it is necessary to have high \( O_2(a) \) yield from the generator, reduce cavity temperature (to reduce \( Y_{OT} \)), reduce losses of \( O_2(a) \) yield, and maintain high efficiencies of laser cavity system components (mixing, extraction, etc.). In COIL, it is also important to have high chlorine utilization \( U_{Cl} \), that is chemical conversion of chlorine gas to oxygen gas (ground state and \( O_2(a) \)). Comparison of Eqns. 9.1 and 9.2 shows that the analog of chlorine utilization in ElectricOIL is instead the ratio of oxygen input flow rate to discharge power input. Similar to the desire for high chlorine utilization in COIL for efficient operation, in ElectricOIL, it is desirable to apply discharge techniques that maintain low power input per oxygen flow rate, while attaining high \( O_2(a) \) yields. The performance of an ElectricOIL discharge should be judged on these grounds:

- \( O_2(a) \) production efficiency, \( \eta_{O2(a)} = Y \frac{\dot{n}_{O2}}{E_{O2(a)}/RF_{sys}} \)
- The rise in gas temperature through the discharge which impacts \( Y_{OT}(T) \)
- The influence the discharge has on loss mechanisms and system component efficiencies (for example, the influence of oxygen atoms on kinetics downstream of the discharge).

### 9.2. Performance of Various ElectricOIL Configurations

Here, the progress in gain and laser power extraction with various ElectricOIL configurations over the years 2004-2008 will be summarized. A generalized ElectricOIL configuration is shown in Fig. 9.1. The system is fed by a supply of oxygen, helium and nitric oxide which is flowed through a RF discharge in which the oxygen is excited to the \( O_2(a) \) state. The discharge effluent passes through a heat-exchanger to remove excess heat, and then mixes with iodine (secondary, carried by helium) and nitrogen (tertiary). The combined flow then passes through a convergent-divergent nozzle, becomes supersonic resulting in significant decrease in temperature, and then passes into a laser cavity with high-reflectivity mirrors on either side. Between the iodine injection and the laser cavity, the iodine is dissociated by energetic species in the flow (oxygen atoms, \( O_2(a) \), \( O_2(b) \)) and
excited to the upper laser level I* by near-resonant transfer with O$_2$(a), with the equilibrium rate favoring I* at low temperature. With sufficient O$_2$(a) yield, a population inversion is maintained in the iodine, and power is extracted in the laser cavity.

**Figure 9.1. Basic schematic of the ElectricOIL system developed by CU Aerospace and the University of Illinois [9.7].**

The configurations detailed in Table 9.1 span the development of ElectricOIL from the first report of lasing at 220 mW (Carroll et al. [9.2], results from 10/2004 experiment) to the most recent publishing of results in summer of 2009 (Zimmerman et al. [9.8], results from 11/2008 experiment). Results with three types of discharges are shown: Longitudinal Capacitively-Coupled RF (LCCRF), Inductively-Coupled RF (ICRF), and Transverse Capacitively-Coupled RF (TCCRF). As reported by Carroll et al. [9.3], fairly similar output power results were obtained at lower pressures (12.5 Torr) with both LCCRF (510 mW) and ICRF (524 mW), with the O$_2$(a) yield produced in the discharge as a function of power deposited being virtually identical.

Optimization of CAV2 with LCCRF discharge operating at 16.5 Torr resulted in raising the total power output to 1.47 W [9.4]. As the device was scaled to higher pressure and flow rate, TCCRF was found to have better O$_2$(a) production qualities than LCCRF, and the device was improved to 4.5 W output with CAV3 [9.5]. The performance of the TCCRF-CAV3 device was further improved by optimization of system flow rates and the use of a pre-dissociation discharge for the I$_2$, and 6.2 W output was measured for 20% less total power input [9.6].
### Table 9.1. Details and performance of various ElectricOIL configurations.

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<td>( O₂(a) ) Yield [%]</td>
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<td>18.0</td>
<td>12.0</td>
<td>16.5</td>
<td>13.5</td>
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<td>Dissociation [%]</td>
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<td>---</td>
<td>1.3 (21 cm)</td>
<td>9.0 (exit)</td>
<td>6.3 (exit)</td>
<td>12.5 (exit)</td>
<td>12.5 (exit)</td>
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<tr>
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<td>180</td>
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<tr>
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<td>6.2</td>
<td>12.3</td>
<td>28.1</td>
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<td>122</td>
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<tr>
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<td>0.127</td>
<td>0.205</td>
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<td>0.175</td>
<td>0.104</td>
<td>0.119</td>
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<td>4.89x10⁻⁴</td>
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<td>2.67x10⁻³</td>
<td>4.5x10⁻³</td>
<td>8.86x10⁻⁴</td>
<td>6.15x10⁻⁴</td>
<td>1.08x10⁻⁴</td>
</tr>
</tbody>
</table>

*Inductive discharge with 6.4 cm long 5 turn coil where the flow volume inside the coil is 121 cm³. Similar laser performance results were obtained with a hollow cathode discharge with a 25.4 cm gap.

A variety of configuration studies with TCCRF investigated the influence of various parameters, primarily pressure, electrode gap, and excitation frequency, on \( O₂(a) \) production performance (as discussed in Section 6). These demonstrated that discharge performance
could be improved by decreasing the discharge gap for increased pressure. Thus a new configuration was constructed using dual transverse discharges in 1.6 cm I.D. tubes along with an improved cavity chamber design CAV4 which reduced the flow distance between the discharge and the iodine injection discharge, and introduced a water-cooled heat-exchanger; with a doubling of system flow rates, this system allowed approximately double the power output of the previous configuration, 12.3 W with 0.17 %/cm gain [9.7]. The heat-exchanger from CAV4 was redesigned, optimized and reapplied in a quad-discharge design with CAV5 which was shorter in flow length than CAV4 and had a larger nozzle throat to allow higher flow rates. This configuration (TCCRF-CAV5) gave gain of 0.22 %/cm and an output power of 28.1 W [9.8].

Figure 9.2 shows power output results as a function of input oxygen flow rate for various discharge configurations. In early development, similar results were obtained with a variety of configurations. However, improvement of ElectricOIL to the current power level proceeded using TCCRF discharges due to the robustness and availability of 13.56 MHz supplies, and the ease of constructing and optimizing TCCRF configurations for good O₂(a) production at high pressures and flow rates. Improvement of laser power output has been due to both improvements in system efficiency and increases in total system flow rate.

Figure 9.2. ElectricOIL power output as a function of oxygen flow rate with various RF discharge configurations using cavities with 5 cm gain length.
9.3. Comparisons of Gain Measurements to BLAZE Modeling

From the data given in Table 9.1, ElectricOIL power output and gain have steadily increased as improvements to various system components have been made. These include

1. optimization of O₂(a) production as system flow-rates and pressures increase
2. improved thermal management by application of heat-exchanger designs
3. reduction of system flow distances to decrease O₂(a) losses
4. optimization of I₂ flow rate to maximize gain
5. optimization of mirror parameters (reflectivity, size) to improve extraction

Understanding the influence of various system parameters is simplified by the use of the BLAZE models developed by Palla to simulate the ElectricOIL end-to-end system dynamics [9.9, 9.10]. The BLAZE models (in various versions) have been used to accurately predict the gain measurements observed in ElectricOIL experiments.

Early experimental results were well replicated by the BLAZE II model which did not model the discharge itself, but instead modeled the post-discharge kinetics beginning with experimentally measured values of excited species at the discharge exit [9.9]. Figure 9.3 shows a comparison of the BLAZE II modeled gain and the gain measurements originally presented by Carroll et al. for CAV2 with a LCCRF discharge [9.3]. The agreement between the two results is excellent. However, the power predicted by the model was high by a factor of 2-4 compared to the measurements of 220-525 mW in this gain range (using 2.54 cm diameter optics) [9.3].

Results from CAV3 were also modeled, using the BLAZE-IV code [9.9]. BLAZE-IV is an end-to-end discharge through laser cavity model that includes electrodynamics for the discharge section and quasi-1D fluid equations with multi-stream mixing terms [9.9]. CAV3 with a TCCRF (49 mm I.D. clamshell) discharge was used to obtain 4.5 W output for the flow conditions 10:33:0.15 mmol/s O₂:He:NO. Simulations of the gain results are shown in Fig. 9.4. This same system was later updated to include an I₂ injector discharge which enhanced the power output to 6.2 W [9.6].
Figure 9.3. Mixing prediction of cavity gain as a function of axial position for varied I₂ flow rate (from [9.9]). The discharge and tertiary flow rates are 3:16:0.15:55 mmol/s O₂:He:NO:N₂. Power measurements with gain in this range resulted in 220-525 mW [9.3].

Figure 9.4. Experimental results and BLAZE-IV simulations for gain in ElectricOIL TCCRF-CAV3 for 10:33:0.15 O₂:He:NO into the discharge operating at 20 Torr, and 1 kW of RF input [9.5]. A photo of the CAV3 nozzle duct is shown in the plot above the data for reference.

Newer configurations applied the use of smaller discharge tubes which offered better O₂(a) production performance at higher pressures [9.7, 9.8]. The compactness of these smaller diameter discharges offered the possibility of using an “array” of discharges in parallel in order to increase the total system flow rate. The first of these was a dual discharge design in which two 16 mm I.D. TCCRF discharge tubes were used in conjunction with a water-cooled heat-exchanger and iodine pre-dissociation discharge to obtain at total output power of 12.3 W [9.7]. The newest results were obtained with the fifth generation laser cavity, CAV5 pictured in Fig. 9.5, that used four 1.6 cm I.D. TCCRF discharges feeding into a single 5 cm gain length laser cavity, as well as compact heat exchangers that reduce both the flow temperature and the concentration of oxygen atoms (see [9.8]). These CAV5 experiments were run without the addition of a secondary RF discharge [9.6, 9.7] to pre-dissociate the molecular iodine.
The total flow conditions for these gain and laser power experiments with the four primary TCCRF discharges were 30:100:0.2 mmol/s O₂:He:NO. A secondary stream of ≈ 0.30 mmol/s of I₂ diluted in 55.0 mmol/s of He diluent was injected 27.8 cm downstream from the exit of the primary discharges. A tertiary flow of 240 mmol/s of cold N₂ gas (≈83 K) was injected further downstream to lower the temperature. The pressures in the discharge section, in the subsonic section downstream of the heat exchanger, and in the supersonic diagnostic cavity were 53.0 Torr, 44.3 Torr, and 4.7 Torr, respectively. Measurements near the exit of the discharge from the O₂(1∆) and O₂(b¹Σ) spectra indicated an O₂(1∆) yield of ≈ 11% and a gas temperature in the range of 570-590 K for these flow conditions at 650 W of RF power in each of the four discharges (a total of 2600 W).

Gain was measured for the above flow conditions at a total of 2.6 kW of primary RF discharge power. Figure 9.6 shows the gain at line center, which peaks at 0.22 %/cm. The lineshape indicates a temperature of ≈ 110 K. For comparison, the best gain previously observed was 0.17% cm⁻¹, using dual 1.6 cm I.D. primary TCCRF discharges with CAV4 [9.7].

This CAV5 case with four TCCRF discharges was also modeled in BLAZE-IV [9.9]. Using the baseline mixing parameters established for the older CAV3 hardware, and simply making changes to the geometry and flow/discharge conditions that are appropriate for this CAV5 case, good agreement was found with the gain measurement, shown in Fig. 9.7, as well as temperature and yield measurements, shown in Fig. 9.8.
9.4. Gain Recovery Measurements

The power extraction issues discovered in modeling ElectricOIL results [9.9] prompted the measurement of gain recovery, which is the gain (proportional to $[I^*]-0.5[I]$) as a function of position downstream of an active resonator [9.11]. The goal of this measurement was to determine whether or not $I^*$ was being re-pumped at the expected rate within the lasing region. The measurement was made using specially designed hardware as sketched in Fig. 9.9. The $O_2(a)$ is produced by a 4.9 cm I.D. TCCRF (13.56 MHz) discharge in $O_2$-He-NO mixture. The $O_2(a)$-rich flow (primary) exiting the discharge region passes
through a water-cooled heat exchanger and then passes through a duct containing injectors for iodine vapor carried by helium (secondary) and cooled nitrogen (tertiary). The combined flow is then expanded through a Mach 2 nozzle which has purged mounts on either side of the supersonic flow section that accept 50 mm (2") optics into which wedged windows can be placed for gain measurements, or laser mirrors can be placed for laser oscillation. For this particular set of experiments, a special insert was manufactured in order to hold a 25 mm high-reflectivity laser mirror at each mount centerline inside of the wedged windows, allowing a gain probe beam to pass upstream and downstream of the active resonator. Two 99.996% reflective mirrors purchased from AT Films, each with 2 m radius of curvature formed a stable optical cavity with a mirror separation of 33 cm and a gain length of 5 cm.

The primary flow conditions for the gain recovery measurements were 7:33:0.05 mmol/s O_2:He:NO. The power input to the discharge was 700 W. The O_2(a) yield measured downstream of the discharge for these conditions was \( \approx 18\% \), which corresponds to 170 W stored in the O_2(a) flow. A secondary stream of \( \approx 0.02 \) mmol/s of I_2 with 20.0 mmol/s of secondary He diluent was injected 32.4 cm downstream from the exit of the primary discharge. Gain recovery measurements were taken for two tertiary N_2 flow inputs: (a) 74 mmol/s N_2 at 140 K, and (b) 50 mmol/s N_2 at 300 K. These flow conditions result in laser cavity temperatures of approximately 115 K and 164 K for cases (a) and (b) respectively. In case (a) the discharge operated at 24 Torr. In case (b) the discharge operated at 20 Torr.

![Illustration of the experimental supersonic cavity apparatus used to measure gain recovery downstream of an active resonator [9.11].](image)

The spatial gain measurements and corresponding BLAZE-V modeling results are shown in Fig. 9.10. The modeling results are shown for two values of the forward pumping rate of the reaction O_2(a) + I ⇌ O_2 + I*. The accepted forward rate for classic chemical
oxygen iodine laser pumping is \( k_f = 7.8 \times 10^{-11} \) molecules\(^{-1}\) cm\(^3\) s\(^{-1}\) (see van Marter and Heaven [9.12]), while the modified effective rate which results in improved agreement with the gain measurements in both cases is \( k_{f, eff} = 1.9 \times 10^{-11} \) molecules\(^{-1}\) cm\(^3\) s\(^{-1}\). In both modeling cases, the backward rate is determined from the well-established equilibrium rate [9.12], \( K_{eq} = k_b/k_f = 1.3346e^{-403/T} \). This 4x reduction in forward rate supports a prior hypothesis by Rawlins et al. [9.13] that there is some important unknown kinetic process that is specific to the ElectricOIL system and tied to the pumping process. The result that the same effective rate constant provided good agreement with both sets of data at different temperatures suggests that this ElectricOIL-specific kinetic process is relatively temperature independent.

![Figure 9.10](null) Comparison of gain data with BLAZE-V predictions as a function of axial location and \( I + O_2(a) \leftrightarrow I^* + O_2(X) \) forward pumping rate for a lower temperature flow with (a) 74 mmol/s of tertiary N\(_2\) injected at 140 K and (b) 50 mmol/s of tertiary N\(_2\) injected at 300 K. This work was originally reported in [9.11].

To reinforce the conclusion from the above comparison of experiment and the BLAZE-V model, the data was compared to a simple analytic model. The spatial derivative of the gain can be expressed as

\[
\frac{dg}{dx} = \frac{d}{dx} \left\{ \sigma(T) \left( [I^*] - \frac{1}{2} [I] \right) \right\} = \sigma(T) \left\{ \frac{d[I^*]}{dx} - \frac{1}{2} \frac{d[I]}{dx} \right\},
\]

(Eqn. 9.3)

where \( \sigma(T) = \frac{7}{12} (1.293 \times 10^{-17}) \sqrt{\frac{300}{T}} \) is the stimulated emission cross-section (in cm\(^3\)), and the spatial derivatives of \([I^*]\) and \([I]\) can be expressed as
\[
\frac{d[I^*]}{dx} = \frac{1}{u} \frac{d[I^*]}{dt} = \frac{1}{u} \left( k_f [O_2(^1\Delta)][I] - k_b [O_2][I^*] - k_q [O][I^*] \right) 
\]  
(Eqn. 9.4)

where the backward rate \( k_b = k_f / K_{eq} \), \( k_q \) is the rate of \( I^* \) quenching by oxygen atoms, and \( u \) is the flow velocity. The influence of oxygen atom quenching is negligible in these cases, and the slope at a given point in the data can be approximated as linear, such that \( dg/dx = C \) is constant. Using these approximations, and the above relations, the effective forward rate can be expressed as

\[
k_{f, eff} = \frac{2uC}{3\sigma(T) \left[ [O_2(^1\Delta)][I] - \frac{1}{K_{eq}} [O_2][I^*] \right]}.
\]  
(Eqn. 9.5)

Using this simple model, and measured values of slope from the gain data in Fig. 9.10, and other inputs to Eqn. 9.5, the values of \( k_{f, eff} \) determined in the (a) chilled and (b) room-temperature \( N_2 \) tertiary cases were \( 1.64 \times 10^{-11} \) molecules\(^{-1}\) cm\(^3\) sec\(^{-1}\) and \( 1.45 \times 10^{-11} \) molecules\(^{-1}\) cm\(^3\) sec\(^{-1}\), respectively. Thus, this simple analytical model is in agreement with the assessment from BLAZE-V calculations that there is an unknown mechanism which competes with the forward pumping of \( I^* \) by \( O_2(a) \).

The measured laser powers were 1.8 W and 0.85 W for data in Figs. 9.10.a and b, respectively. The predicted laser powers using a forward rate of \( k_f = 7.8 \times 10^{-11} \) molecules\(^{-1}\) cm\(^3\) sec\(^{-1}\) were 9.2 W and 5.2 W for Figs. 9.10.a and b, respectively. When the forward rate was reduced to \( k_{f, eff} = 1.9 \times 10^{-11} \) molecules\(^{-1}\) cm\(^3\) sec\(^{-1}\) the predicted laser powers were reduced to 3.6 W and 1.7 W for Figs. 9.10.a and 9.10.b, respectively. Compared to the experiment, the BLAZE-V model predicts a similar ratio of power outputs between the cold and room-temperature tertiary flow conditions as that observed in the experiment (the power output in the room-temperature \( N_2 \) case is approximately 50% of the chilled \( N_2 \) case), but the predicted powers are still higher than measured, even when the reduced pumping rate which agrees with the gain recovery measurement is used. Therefore, the low measured powers are likely due to the combined effects of a slow effective pumping rate and optical losses.
9.5. Modified Rigrod Theory (from Carroll and Verdeyen)

Although the gain recovery measurements explain some of the power extraction issues observed in ElectricOIL, there was still significant discrepancy between the measured power and the power predicted by the BLAZE model (using Fabry-Perot optics with similar mirror reflectivities, transmissions, and flow residence times to the experiment), while the gain measurements were well replicated (see section 9.3). In addition, interpretation of the gain recovery results is complicated considering that the $[O_2(a)]$ in the cavity region is not well established, and may be over-predicted (or under-predicted) by the model; as dictated by the simple model of Eqn. 9.5, the observed effective rate is inverse with $[O_2(a)]$, and therefore over-predicting the cavity yield would result in a reduced effective rate.

Another factor which was thought to be a deficiency in power extraction was optical losses. Scattering losses with new high-quality laser mirrors were thought to be small, but another possibility was loss due to diffraction. This was studied analytically by Carroll and Verdeyen [9.12] using Rigrod theory [Rigrod, 9.13] modified to include an aperture loss term accounting for Fraunhofer diffraction that occurs off the edges of the supersonic cavity. Carroll and Verdeyen applied this modified theory to laser power data taken with both the 4-discharge tube ElectricOIL system described here (TCCRF-CAV5 [9.8]), and VertiCOIL data taken by Rittenhouse et al. [9.14], achieving good agreement with both data sets.

The modified Rigrod theory developed by Carroll and Verdeyen [9.12] results in the equation for output power $P_{out}$ as a function of mirror reflectivities $r_1$ and $r_2$, mirror transmissivities $t_1$ and $t_2$, small signal gain $g_0$, gain length $L_g$, and mirror area $A$,

$$P_{out} = I_{sat} \frac{(1-\delta)}{\sqrt{r_1} + \sqrt{r_2}} \left[ g_0 L_g + \ln\left(\frac{(1-\delta)}{\sqrt{r_1/r_2}}\right) \right] A,$$

(Eqn. 9.6)

assuming the diffraction loss term $\delta$ is the same on both sides of the resonator. The saturation intensity $I_{sat}$ can be estimated from the detailed analytical model provided by Hager et al. [9.15].

The multi-discharge tube ElectricOIL system TCCRF-CAV5 pictured in Fig. 9.5 was tested for peak power with five mirror combinations shown in Table 9.2. The power output as a function of $r_1r_2$ is compared to the modified Rigrod theory in Figure 9.11, using the inputs $P_{sat} = I_{sat}A = 5940 \text{ W}$, $g_0 = 0.002 \text{ cm}^{-1}$, $L = 5.0 \text{ cm}$, $a = 2 \times 10^{-5}$, $t = 1-r-a$, and $\delta = 5.3 \times 10^{-4}$. In this particular analysis (taken from [9.12]), $\delta$ was computed from the aperture of
the resonator geometry, and $I_{sat}$ was chosen to give the best fit to the laser data. The classical Rigrod theory overestimates the peak output power significantly, while use of the Rigrod theory modified to account for diffraction losses is in good agreement, and predicts peak output power of $\sim 34$ W. The effect of the diffraction term is to both lower the peak power and shift the peak to lower values of $r_1 r_2$. Laser power output as a function of RF power input is shown in Fig. 9.12 for the mirror combinations listed in Table 9.2. As the mirror reflectivity product decreases, the gain threshold required for laser increases ($g_{th} = -\ln(r_1 r_2)/2L_g$), and therefore the RF power required for laser threshold increases. The peak gain at 2.6 kW was 0.22 %/cm.

Table 9.2. Mirror combination sets used in test of ElectricOIL CAV5 / quad-discharge tube configuration.

<table>
<thead>
<tr>
<th>Set</th>
<th>Mirror 1</th>
<th>Mirror 2</th>
<th>$r_1$</th>
<th>$r_2$</th>
<th>$g_{th}$ = $f(r_1 r_2)$ [cm$^{-1}$]</th>
<th>$P_{out, max}$ [W]</th>
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<td>0803-1</td>
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<td>0.998837</td>
<td>1.870x10$^{-3}$</td>
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<tr>
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<td>0802-1</td>
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<td>0.989620</td>
<td>1.048x10$^{-3}$</td>
<td>22.3</td>
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<tr>
<td>4</td>
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<td>0802-1</td>
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<td>0.989620</td>
<td>1.055x10$^{-3}$</td>
<td>23.2</td>
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<tr>
<td>5</td>
<td>0803-1</td>
<td>0802-1</td>
<td>0.999837</td>
<td>0.989620</td>
<td>1.160x10$^{-3}$</td>
<td>19.7</td>
</tr>
</tbody>
</table>

Figure 9.11. Comparison of recent ElectricOIL power data and the modified Rigrod theory of Carroll and Verdenyen. The total outcoupled power is plotted versus the product of the mirror reflectivities, $r_1 r_2$. The parameters used in the Rigrod theory were $P_{sat} = I_{sat} A = 5940$ W, $g_0 = 0.002$ cm$^{-1}$, $L_g = 5.0$ cm, $a = 2x10^{-5}$, $t = 1-r-a$, and $\delta = 5.3x10^{-4}$.

Figure 9.12. ElectricOIL output power as a function of RF input power for varied mirror sets shown in Table 9.2. From initial slopes of these data and the threshold gain determined for each mirror set, gain as a function of RF power near threshold can be determined. For example the data from mirror sets 3 and 4 suggest that the gain is $\sim 0.105$ %/cm at $\sim 1.55$ kW compared to the probe-measured value of 0.22 %/cm at 2.6 kW.
9.6. Discussion about Overall ElectricOIL Performance

At this point, the major issue in ElectricOIL development is improving laser efficiency. Although it is difficult to compare electrical efficiency in ElectricOIL to chemical efficiency in COIL, it is easy to compare yield losses, cavity temperature conditions, and extraction efficiencies. The overall efficiency of an ElectricOIL device can be broken down into 4 categories: (1) \( \eta_{O_2(a)} \) production efficiency, (2) \( \eta_{\text{trans}} \) transport efficiency, (3) population inversion efficiency \( \eta_{\text{inv}} \) and (4) cavity “system” efficiency \( \eta_{\text{sys}} \) (including mixing, geometric, residence time, and extraction). Eqn. 9.2 can be rewritten

\[
\eta_{\text{elec}} = \frac{P_{\text{out}}}{E_{\text{RF}_{\text{sys}}}} = \frac{E_{I^*}}{E_{O_2(a)}} \cdot \left( \frac{\dot{Y}_{O_2} - E_{O_2(a)}}{RF_{\text{sys}}} \right) \cdot Y \left( 1 - \frac{Y_{\text{loss}}}{Y_{\text{OT}(T)}} \right) \cdot \eta_{\text{sys}}, \quad \text{(Eqn. 9.3.a)}
\]

where the new parameters are

\[
\eta_{\text{trans}} = 1 - \frac{Y_{\text{loss}}}{Y} \quad \text{(Eqn. 9.3.b)}
\]

\[
\eta_{\text{inv}} = \frac{Y - Y_{\text{loss}} - Y_{\text{OT}(T)}}{Y - Y_{\text{loss}}} \quad \text{(Eqn. 9.3.c)}
\]

\[0.965 = \frac{E_{I^*}}{E_{O_2(a)}}\] is the exothermic loss of the pumping reaction. The parameter \( \eta_{\text{trans}} \) represents the efficiency of transporting \( O_2(a) \) from the discharge to the resonator, or the fraction of the yield that survives the trip to the cavity. \( \eta_{\text{inv}} \) represents the efficiency of using the yield that reaches the cavity, or the fraction of power stored in the \( O_2(a) \) that is available for extraction.

Determination of \( \eta_{\text{elec}} \) is simple, and \( O_2(a) \) production efficiency \( \eta_{O_2(a)} \) is readily known from calibrated 1268 nm measurements near the discharge exit (see Table 9.1). \( Y_{\text{OT}(T)} \) is known from temperatures determined from gain profile measurements. \( Y_{\text{loss}} \) is the most difficult parameter to determine, but it can be calculated from measurements of the gain, temperature, and iodine flow rate using the method devised by Hager [9.16], Davis and Rawlins [9.17], or it can be estimated at laser power threshold conditions if the cavity temperature is known. Also, \( Y_{\text{loss}} \) can be taken from modeling cases as shown above in Section 9.3. Given \( Y_{\text{OT}} \) and \( Y_{\text{loss}} \), \( \eta_{\text{trans}} \) and \( \eta_{\text{inv}} \) are easily calculated and \( \eta_{\text{sys}} \) can be determined from Eqn. 9.3.a.
Table 9.3 gives the breakdown of efficiencies based on some of the experimental cases reported in Section 9.2 and modeled in Section 9.3. For reference, values determined for RotoCOIL by Hon et al. [9.1] are included; a forecasted version of ElectricOIL is also shown assuming efficient discharge production of \( O_2(a) \) based on best yields and efficiencies seen in experimental cases, and assuming that \( \eta_{sys} \) similar to those in RotoCOIL can be attained.

Table 9.3. Efficiency breakdown of various ElectricOIL configurations compared to RotoCOIL analysis by Hon et al. [9.1] and forecasting of ElectricOIL to similar output based on possible efficiency numbers.

<table>
<thead>
<tr>
<th>System</th>
<th>ElectricOIL</th>
<th>COIL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LCCRF CAV2</td>
<td>LCCRF CAV2</td>
</tr>
<tr>
<td>Reference</td>
<td>[9.3]</td>
<td>[9.3]</td>
</tr>
<tr>
<td>( \dot{\nu}_{cl} ) ( \dot{E}_r )</td>
<td>450 W</td>
<td>450 W</td>
</tr>
<tr>
<td>( O_2)He:NO \ [mmol/s]</td>
<td>3:16:0.15</td>
<td>3:16:0.15</td>
</tr>
<tr>
<td>( I_2)He \ [mmol/s]</td>
<td>0.022:3</td>
<td>0.036:3</td>
</tr>
<tr>
<td>Mirror Dia. \ [cm]</td>
<td>2.54</td>
<td>2.54</td>
</tr>
<tr>
<td>( \eta_{O2(a)} )</td>
<td>0.107</td>
<td>0.107</td>
</tr>
<tr>
<td>( Y ) \ [%]</td>
<td>17.0</td>
<td>17.0</td>
</tr>
<tr>
<td>( Y_{loss} ) \ [%]</td>
<td>6.8</td>
<td>2.2</td>
</tr>
<tr>
<td>( T_{cav} ) \ [K]</td>
<td>160</td>
<td>190</td>
</tr>
<tr>
<td>( Y_{OT(T)} ) \ [%]</td>
<td>5.1</td>
<td>7.4</td>
</tr>
<tr>
<td>( \eta_{trans} )</td>
<td>0.600</td>
<td>0.870</td>
</tr>
<tr>
<td>( \eta_{inv} )</td>
<td>0.500</td>
<td>0.500</td>
</tr>
<tr>
<td>( \eta_{sys} )</td>
<td>0.019</td>
<td>0.022</td>
</tr>
<tr>
<td>( \eta_{elec} or (\eta_{chem}) )</td>
<td>5.78x10^-4</td>
<td>9.78x10^-4</td>
</tr>
<tr>
<td>( P_{out} ) \ [mW]</td>
<td>260 mW</td>
<td>440 mW</td>
</tr>
</tbody>
</table>

When comparing the efficiencies of ElectricOIL and RotoCOIL, it is evident that ElectricOIL is lacking primarily in \( \eta_{sys} \) and \( \eta_{O2(a)} \). The inversion efficiency \( \eta_{inv} \) is low, but this will improve if the level of yield from the discharge can be improved while maintaining low losses and cavity temperatures similar to those in recent experiments with CAV4 and CAV5. Recent experiments and modeling indicate that the level of \( O_2(a) \) yield possible should be in the range of 25-30%, and that these yields can be attained with a well-designed discharge with 30% efficiency. It is likely that no further improvements in discharge production of \( O_2(a) \) will be possible, although recent experiment from researchers at Physical
Sciences Inc. indicate a catalytic effect that may result in substantial $O_2(a)$ yield improvement [9.18]. So, the major problem to solve is the cavity system efficiency which includes the mixing, geometric, residence time, and extraction efficiencies associated with the cavity. From Table 9.2, $\eta_{sys}$ has increased significantly, but further improvement (~factor of 3) will be required to attain similar efficiencies to COIL devices.

From various recent studies discussed in the previous subsections, three major issues should be addressed in future ElectricOIL work to improve efficiency: (1) The gain recovery measurements shown in Section 9.4 suggest that the low extraction efficiency is associated with slowed kinetic re-pumping rates of $I^*$ (due to an unknown mechanism). This can be resolved in future work by design of the resonator to increase the residence time (for example use of larger mirrors, or a folded-axis resonator design), or by resolving the kinetics which cause the effect and determining a way to eliminate the effect. (2) The recent work with Rigrod theory modified to include diffraction losses (Section 9.5) indicates that a significant amount of inefficiency is associated with optical losses. This problem should be eliminated as the gain of ElectricOIL is improved, and the diffraction loss becomes less significant. (3) Improvements to transport efficiency $\eta_{trans}$ would also result in significant performance gains; from the modeling of CAV5 in Fig. 9.8 (Section 9.3), it is obvious that a substantial amount of the power stored in $O_2(a)$ is lost between the iodine injection region and the nozzle throat where the losses due to $I^* + O \rightarrow I + O$ reaction are significant due to the residence time in the subsonic region after $I_2$ injection. This issue should be addressed in future designs and experiments, perhaps by the removal of oxygen atoms by NO$_2$ titration, and replacing the oxygen atom $I_2$ dissociation mechanism with a secondary discharge for $I_2$ pre-dissociation discharge which has shown promising results in initial studies [9.6, 9.7].

References


10. Concluding Remarks

A variety of diagnostic techniques have been applied in this work to study the behaviors of radio-frequency discharges in oxygen-helium mixtures intended for use in electric-oxygen iodine lasers (ElectricOIL). These include various optical diagnostics for measuring important species [O_2(a), O_2(b), O, O_3, etc.], a microwave interferometer for measuring electron density, and voltage and current probes for measurements of terminal characteristics. Diagnostics developed for measuring O-atoms (airglow methods, and actinometry) were of particular importance, considering that in early work O-atoms were found to play an important dual role in the ElectricOIL system, influencing both the dissociation of injected I_2, and quenching of energy stored as O_2(a). Given the ability to produce significant O_2(a) flows with robust RF discharge techniques, and control O-atom flow rate by titration with NO_X, it was possible to begin investigating improvements to ElectricOIL technology, and part of this investigation was to develop discharge techniques which could produce significant O_2(a) levels at increased oxygen flow rate and increased operating pressure. The discharge configuration which proved best-fit to this task was transverse capacitive-coupled RF (TCCRF), and the performance of this type of a discharge was analyzed for a range of pressure, gap, and operating frequency. With improvements to the discharge performance, in particular the total system flow rate of O_2(a), it was possible to improve total power output. The laser power extraction was as high as 28 W for a 5 cm gain length and 50 mm optics, and has now been more recently increased to >100 W with further improvements to TCCRF discharges, and use of larger volume folded-resonator techniques ([Woodard et al. 2010 Opt. Lett. 35 1611-1613], see Sect. 9).

At the current state of ElectricOIL technology, O-atoms are still an issue for a variety of reasons:

(i) significant discharge power is devoted to O_2 dissociation (a power loss),
(ii) the O_2(a) production in the discharge is coupled to the O_2 dissociation level,
(iii) O-atoms remove energy stored in O_2(a) by direct quenching (2-body and 3-body mechanisms), and also rapidly when I_2 is introduced [via near-resonance of O_2(a)
\[ \Leftrightarrow I^*, \text{ and } I^* + O \rightarrow I + O \], and
(iv) O-atoms rapidly dissociate I_2, relieving losses of O_2(a) and O_2(b).
Therefore, the level of O-atoms in both the discharge and in the I₂ mixing zone is critically important, and will continue to be an issue in ElectricOIL development.

Fortunately, there are a number of diagnostic techniques available for O-atom measurements. In early work, the use of NO₂ titration proved useful in deducing the role of O-atoms especially in the I₂ mixing kinetics. However, application of this method proves complicated when applied at high pressure and in situations when NO is already present in the discharge flow, due to 3-body recombination kinetics. Furthermore, it gives a result at only one point in the flow, cannot be applied within the discharge, is invasive [changes the flow composition of O, O₂(a), etc.], and it requires the use of NO₂ flow rates which are similar to the oxygen flow rate. These problems led to the use of the calibrated PMT measurements of airglow (due to O-NO recombination), and trace argon actinometry (TAA). Monitoring the O-NO recombination with a calibrated PMT proves very effective given that ElectricOIL discharge flows typically contain trace amounts of NO. However care must be taken to account for the airglow temperature dependence, considering the significant variation of temperature possible in the region downstream of the discharge (300-700 K). The TAA method, applied in either the primary discharge or in a low-power secondary discharge was also an effective technique, but this method does have some issues: (i) currently an airglow technique is required for calibration, and (ii) the method relies heavily on cross-section data and quenching rates of the Ar* and O* states by the background gases (O₂, He, NO). A quick, reliable method for measuring the discharge $E/N$ over a range of operating conditions would be a helpful in applying TAA.

The first measurements of gain and laser in an electric oxygen-iodine laser [Carroll et al. 2005 Appl. Phys. Lett. 86 111104] were made using a longitudinal capacitive-coupled RF (LCRRF) discharge produced in a 50-mm flow tube, with a hollow cathode spacing of 25.4 cm. Early work with this discharge (Sect. 5) demonstrated that the O₂(a) production scaled with specific power deposition $W$ (RF input power divided by input flow rate of oxygen), with the most efficient production occurring for $W < 50$ J/mmol, but the highest yields occurring at approximately $W = 100$ J/mmol. This type of discharge was also used to demonstrate a very significant increase in O₂(a) production when trace NO was added to the flow, and that O₂(a) yield could be optimized by O₂:He diluent ratio. Work with this discharge at varied frequencies demonstrated that O₂(a) yield at high power input could be
improved by increasing the operating frequency from the typical 13.56 MHz (to reduce sheath losses). However, operation of this discharge configuration above approximately 20 Torr proved difficult, and the discharge was prone to arcing instabilities.

Transverse capacitive-coupled RF (TCCRF) were compared to LCCRF, and shown to have similar performance at ~12.5 Torr (operating point of first laser demonstrations). Work discussed in the literature, and initial work by UIUC/CUA with TCCRF discharges suggested that these would be well-suited for high-pressure operation which was desired for overall system performance. Further investigation of TCCRF discharges discussed here showed that the O$_2$(a) produced was a strong function of pressure, gap, and frequency (Sect. 6). These parameters establish the operating current density of the discharge, which influences O$_2$(a) production and dissociation (via residence time, and power density). For example, the higher the operating frequency, the higher the normal mode current density.

The best approach for optimizing O$_2$(a) efficiency in TCCRF is to encourage a normal homogeneous ($\alpha$-mode) discharge with low power density. Operating discharge in abnormal mode (electrodes filled with plasma; power density, current density, terminal voltage increase with power) decreases the O$_2$(a) production efficiency. From plasma intensity measurements, it is evident that this is caused by increased voltage drop across the sheaths, creating conditions which are unfavorable for O$_2$(a) production (high electron temperature near walls). Attempts to alleviate this problem by operating at higher frequency in order to thin the sheath region resulted in another problem; because higher frequency operation allows support of higher current (power) density in the transverse gap, the normal-mode discharge tends to constrict as frequency is increased. This higher power density operation proved to be unfavorable for O$_2$(a) production, and tended to increase the O$_2$ dissociation rate. Therefore, the discharge conditions are very sensitive to gap and frequency, and the typical 13.56 MHz excitation frequency (where numerous multi-kW power supplies are available) works well for discharge operation in the 40-50 Torr range, and a gap of 1.6 cm.

A microwave interferometer (MWI) was applied for the first time to measure electron density and collision frequency in a TCCRF ElectricOIL discharge (Sect. 8). Initial results with this technique were promising; the $E/N$ and current density of measurements in the abnormal discharge were in good agreement with the results deduced from terminal voltage
and current measurements. However, given that ElectricOIL discharges operate in a region where the characteristic frequencies of the plasma (plasma frequency and collision frequency) are on the order of the available microwave frequency (4.1 GHz), the results corresponded to high attenuations and small phase shifts, and the power range over which the interferometer could be applied without reaching “cutoff” conditions was small. Therefore, it is suggested that any further work with MWI make use of a higher microwave frequency (X or Ku band).

Gain and laser oscillation were achieved with the discharge technology capable of significant \( \text{O}_2(\text{a}) \) production (~16%), and the use of NO\(_X\) to control O-atoms. The advancement of the discharge technology to higher pressure, higher flow rate operation has been crucial; the power extraction has improved as the system flow rate and power input have increased (with improvements in overall efficiency from ~0.1 %, to ~3.0 % between CAV2 demonstrations and current CAV6 technology [Woodard \textit{et al.} 2010 \textit{Opt. Lett.} \textbf{35} 1611-1613]). However, from modeling the ElectricOIL with the BLAZE model (with Fabry-Perot optics), the experimentally extracted power is significantly lower than expected. Two factors are shown to be causes of this problem: (i) diffraction losses illustrated through modified Rigrod analysis, and (ii) slower than expected re-pumping of \( \text{I}^* \) demonstrated by gain recovery measurements. The first issue of diffraction losses should become less of a factor as the gain lengths of ElectricOIL devices increase and intracavity flux decreases. However, the mechanism causing the second issue of slower re-pumping of \( \text{I}^* \) (by an effective factor of 4x) remains unidentified, and the effect has continued to be demonstrated in the new system capable of 100 W output [Zimmerman \textit{et al.} 2010 \textit{AIAA Paper} 2010-5038], operating at significantly higher flow rates than the gain recovery experiment discussed in this thesis (Sect. 9.4). If the unidentified mechanism(s) responsible for slow gain recovery in ElectricOIL could be discovered and circumvented, the power efficiency would be significantly improved.

It would be interesting to see the gain recovery measurement repeated in a few scenarios: (i) in a device operating at different Mach number, (ii) in a device where \( \text{O}_2(\text{a}) \) is supplied by another type of discharge, (iii) in a device where \( \text{O}_2(\text{a}) \) is generated chemically. If gain recovery was measured in the EOIL device at Ohio State University [Bruzzese \textit{et al.} 2010 \textit{AIAA Paper} 2010-5039], which operates at Mach 3, the effect will likely be very
significant due to both higher flow velocities, and lower cavity densities. A demonstration of slow re-pumping of I* in that system might explain the lower extraction efficiencies observed at Ohio State compared to the Mach 2 devices at UIUC/CUA. Demonstration of a system operating at Mach number < 2 showing higher extraction efficiency with more rapid gain recovery would also be an informative result. Gain recovery measured in a device using a different type of discharge would confirm whether or not the slow re-pumping is caused specifically by some (unknown) species created in RF discharge, or establish that the issue is associated with electric discharge pumping in general. Gain recovery measured in a chemical oxygen-iodine laser device would establish validity of the kinetics model. In addition, if the level of O2(a) in the chemical system could be reduced to molar fractions similar to EOIL, it might be possible to determine if the observed slow re-pumping / poor power extraction is a rarefied gas effect.

The key findings of this thesis work can be summarized as follows:

- **The parameters which drive O2(a) production in moderate pressure transverse RF discharges in O2/He/NO mixture were investigated.** Pressure, geometry (gap), and frequency drive the characteristic modal behaviors of transverse discharges, and therefore these same parameters influence O2(a) production. These three parameters can be adjusted (in unison) to maximize O2(a) performance. In particular, this involves tuning these parameters to encourage a homogeneous discharge.

- **Electrical parameters (E/N, ne) of RF discharge in typical ElectricOIL O2/He mixture were studied using terminal V-I measurements and a microwave interferometer (MWI).** Comparison of the two methods led to good agreement in current density and plasma E/N. This is the first time that MWI has been applied to ElectricOIL-type discharges, and the work has established that this diagnostic tool may be useful in future discharge design work, and in comparison to discharge modeling.

- **The influence of nitric oxide on O2(a) and O-atoms was studied.** NO can be used to effectively control dominant quenching species (O, O3). Investigation of the “boost” in O2(a) observed with NO has shown that this effect is due primarily to quencher removal and adjustment of [O2(a)]/[O2(X)] for improved O2(a) pumping in the discharge, and not due to the impact on electrical characteristics (E/N).
- **Power extraction issues associated with ElectricOIL technology were investigated by measuring the gain recovery slope downstream of a resonator.** In comparison to modeling, the recovery rate is slower than expected, corresponding to an effective 4x slowing of the forward and backward rates of the pumping reactions. This suggests an additional unidentified mechanism which competes with the pumping reaction.

There are several additional future work studies that might be beneficial to EOIL progress. Some of these are underway, for example I₂ pre-dissociation and folded resonator studies. Additional studies involving the discharge specifically could lead to further enhancement.

One aspect that has not been resolved experimentally in RF discharge is the relationship between discharge $E/N$ and O₂(a) pumping efficiency. The BLAZE modeling illustrates the discharge $E/N$ dictates the O₂(a) pumping efficiency, and that optimal is dependent on the level of O₂(a) due to super-elastic collisions. An optical diagnostic for determining $E/N$ of the bulk plasma based on atomic emission line ratios in a variety of conditions would allow for more accurate modeling of discharge processes, and perhaps allow insight into discharge design for optimal $E/N$. Some optical techniques based on two-line ratios were investigated here, but proved only partially successful. The line ratios of atomic states [e.g. O*(844-nm)/O*(777-nm) or Ar*(751.5-nm)/Ar*(750.4-nm)] were observed to change with added NO, but the magnitude of the experimentally measured ratio was not consistent with the modeled results, likely due to the sensitivity of the method to the relative cross-section shape near threshold. A technique using lines from dual noble gases (Ar and Ne) was suggested (Sect. 7.3).

Another study could involve investigating methods of O-atom suppression in the discharge. In Sect. 7.2 and in modeling, it was shown that controlling O-atom recombination with NO influences O₂(a) production in the discharge, and the lifetime downstream of the discharge. Controlling the O-atoms with NO has been fairly effective, but the influence that NO has on discharge O₂(a) production depends on the ratio between power density (dissociation rate) and density of recombination partners (recombination rate). Because of this, NO becomes less effective at enhancing O₂(a) production when power density increases (due to discharge geometry changes), but operating pressure is held constant. If other effective methods of O-atom suppression can be devised and implemented, construction of
O₂ discharges where the O₂(a) yield more closely approaches the theoretical limit might be possible.

A third suggestion for future work is to re-initialize the ElectricOIL discharge configuration study. Fundamentally, the most progress in laser output has come from increasing the input flow rate of oxygen, and depositing enough power to maximize the O₂(a) yield [and therefore the power carried in the O₂(a) flow]. The transverse capacitive-coupled discharge has been chosen for ElectricOIL mainly because of robustness, and the availability of power supplies at 13.56 MHz. Some other techniques, for instance pulsed-sustainer discharges, were not as far advanced mostly due to the time-commitment for development and the delicacy of the circuitry involved. Further, the modeling indicates that the pulsed-sustainer (designed to reduce $E/N$) will operate in a non-optimal regime as the O₂(a) yield in the flow increases [Carroll et al. 2008 Proc. SPIE 7131 71310B]. However, there are other robust techniques for depositing power into O₂ that might be worth considering, now that the viability of ElectricOIL has been established with transverse RF. These include but are not limited to:

- high-power microwave cavity discharges
- robust pulse-sustainer concepts (pulsed DC-RF sustainer, pulsed RF)
- dual-frequency RF concepts
- hybrid RF-DC discharges
- laser spark-initiated discharges

If further work with ElectricOIL along these lines is continued, the use of small-scale systems to conduct these studies is recommended. Investigating any of the above suggestions at the current scales of EOIL technology (input power at multiple kilowatts, and O₂ flow at 10s of mmols) would not be particularly cost-effective. Operating pressure will be a key issue in development of any of these (optical $E/N$ diagnostic, O-atom suppression, advanced discharges, etc.), but it should be possible to design adequate, informative, small-scale experiments operating at reduced mass flows and power levels, and exploit the useful knowledge obtained in larger scale systems.
Appendix A: O$_2$(a) Density Calibration Experiment

The following describes an experimental procedure for calibration of the 1268-nm emission of O$_2$(a) to [O$_2$(a)] (Method #2 in Sect. 4.1.1).

A.1. Theory

The technique for determining O$_2$(a) yield from iodine 1315-nm absorption/gain measurements was first described by Rawlins et al. [A.1] and derived by Carroll et al. [A.2]. The method relies on the equilibrium between O$_2$(a) and I* to develop a relationship for O$_2$(a) yield as a function of atomic iodine donor density $D_0$, gain density $G$ ($G = [I^*] - 0.5[I]$) and temperature. The equilibrium relationship is

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

(Eqn. A.1)

where

$$
Y = \frac{[O_2(a)]}{[O_2(X)]+[O_2(a)]}, \quad K_{eq} = 0.75 \exp(402/T).
$$

The gain density is related to the peak gain coefficient $\gamma$ by

$$
G = \frac{12}{7} \left( \frac{\gamma}{\sigma_{II}(T)} \right) = \frac{12}{7} \left( \frac{\gamma}{1.293 \times 10^{-17} \sqrt{300/T}} \right) = [I^*] - \frac{1}{2}[I]
$$

(Eqn. A.2).

The iodine donor density is twice the I$_2$ density and is related to [I*] and [I] by conservation of atoms;

$$
fD_0 = 2f[I_2]_{input} = [I^*] + [I]
$$

(Eqn. A.3).

In Eqn. A.3, $f$ is the iodine dissociation fraction. Manipulating Eqns. A.2 and A.3, [I*] and [I] can be expressed in terms of $D_0$ and $G$;

$$
[I] = \frac{2}{3} (fD_0 - G), \quad [I^*] = \frac{1}{3} (fD_0 + 2G)
$$

(Eqn. A.4).

Substituting Eqn. A.4 into Eqn. A.1 results in the equation for O$_2$(a) yield,

$$
Y = \frac{(fD_0 + 2G)}{fD_0(2K_{eq}+1) - 2G(K_{eq} - 1)}
$$

(Eqn. A.5).
A.2. Experiment and Results

Determining the O$_2$(a) yield from Method #2 (see Subsection 4.1.1) requires measurements using a variety of diagnostics described in Sections 4.1-4.4.

1) OMA-V / 0.3-m spectrometer (OMA #2) for measurement of 1268 nm emission of O$_2$(a) and 1315 nm emission of I$^*$ (using 600 µm Thorlabs multimode fiber collection)

2) Apogee CCD / 150-mm spectrometer for measurement of 762 nm emission of O$_2$(b) (and temperature)

3) PSI Gain Diagnostic (ver. 3) to measure gain $\gamma$ and gain temperature $T_g$

4) PSI Microabsorbance Monitor to determine I$_2$ flow rate

5) Santa Barbara Instruments Group (SBIG) CCD / 150-mm spectrometer tuned to 576.2 nm to measure the LIF of I$_2$ by 514 nm Ar-Ion laser and determine I$_2$ dissociation fraction $f$

6) Calibrated airglow measurements with PMT to determine oxygen atom flow rates

A sketch of the experimental setup is shown in Fig. A.1.

![Figure A.1. Setup used for O$_2$(a) calibration experiment (Method #2).](image-url)

The data was taken with RF input between 500 and 900 W, with a primary mixture of 10:33:0.16 mmol/s O$_2$:He:NO at ~21 Torr. The iodine flow rate was between 7 and 13 µmol/s (decreased during the experiment, which took roughly an hour to complete). For these conditions, the LIF measurements confirmed full dissociation of I$_2$ (this data was shown in Fig. 4.5). The temperature (from gain profile and O$_2$(b)) and gain (absorption) measurements for these conditions are shown in Fig. 4.6; O$_2$(b) and gain measurement were
in good agreement (within 10%), but the gain measurement was used in calculations. The resulting equations for \([O_2(a)]\) and \([I^*]\) respectively are

\[
[O_2(a)] = [O_2(X)] \frac{Y}{1 - Y}, \quad \text{(Eqn. A.6)}
\]

\[
[I^*] = \frac{1}{3} \left( fD_0 + 2G \right) \quad \text{(Eqn. A.7)}
\]

In these calculations it is important to use the airglow measurements of oxygen atoms to properly determine \([O_2(X)]\), and to verify that \([O_2(b)]\) was negligible. A comparison of the densities calculated using Eqns. A.6 and A.7 is with the measured intensities at 1268 nm and 1315 nm respectively is shown in Figure A.2. This resulted in a calibration factor for \(O_2(a)\) of

\[
F_{\text{cal},O_2(a)} = 1.13 \times 10^{13} \text{ cm}^{-3}/(\text{counts/s})
\]

denoting the diagnostic setup used. The calibration factor for \(I^*\) obtained comparing 1315-nm emission and \([I^*]\) was

\[
F_{\text{cal},I^*} = 5.41 \times 10^8 \text{ cm}^{-3}/(\text{counts/s})
\]

Figure A.2. Results from \(O_2(a)\) calibration experiment using Method #2 (see Subsection 4.1.1): (a) measured 1268-nm intensity and calculated \([O_2(a)]\) (b) measured 1315-nm intensity and calculated \([I^*]\).

References
