Next Generation Diagnostics for COIL: New Approaches for Measuring Critical Parameters

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Next generation diagnostics for COIL: new approaches for measuring critical parameters

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ABSTRACT

In this paper we discuss several sensitive diagnostics that have been specifically developed for application to COIL and other iodine laser concepts such as AGIL and DOIL. We briefly cover the history of some important diagnostics including recently–developed diode laser sensors for a variety of parameters including: water vapor concentration, singlet oxygen yield, small signal gain, and translational temperature. We also discuss new developments and extensions of prior capabilities including: an ultra-sensitive diagnostic for I2 dissociation, a new monitor for singlet oxygen yield, and a novel diode laser-based imaging system for simultaneous, multipoint spatial distributions of species concentration and temperature. Finally, we mention how these diagnostics have been successfully applied to the emerging DOIL technology.

Keywords: chemical oxygen iodine laser, optical diagnostics, small signal gain, translational temperature

1. INTRODUCTION

The chemical oxygen iodine laser (COIL) was the first in a unique class of atomic transition lasers pumped by energy transfer from a metastable partner. In COIL, the \( ^3P_{1/2} \) state of iodine is excited by energy transfer from singlet molecular oxygen \( (O_2(a^1\Delta)) \) that is produced by a two phase chemical reaction. As detailed elsewhere in this volume, the reaction of Cl2 with a basic hydrogen peroxide evolves gaseous singlet oxygen that is then used to excite the atomic iodine. COIL represents a unique class of gas phase lasers that has undergone tremendous development since it was first demonstrated in 1978 by McDermott et al.1 Even though the laser transition in COIL involves only two spin orbit terms in the ground state iodine energy manifold, the laser presents many challenges and some seemingly basic phenomena are not yet understood.

Modern COIL systems are supersonic mixing devices in which molecular iodine is injected into a flow of singlet molecular oxygen that also contains some water vapor, an unavoidable by product of the singlet oxygen generator (SOG). Water vapor and heat are both deleterious to efficient COIL operation. Thus, there was an early requirement for diagnostics for water vapor and translational temperature.

The mechanism of the molecular iodine dissociation by the singlet oxygen is perhaps the most long standing problem in COIL and it is still not understood. The early work of Derwent and Thrush2,3 hypothesized that \( O_2(b^1\Sigma) \) had sufficient energy to dissociate the molecular oxygen, but this became problematic as an explanation in COIL because the chemical generator produces no \( O_2(b^1\Sigma) \) directly. In addition, any singlet sigma oxygen produced by subsequent energy pooling of two singlet delta molecules is rapidly quenched by water vapor. Detailed kinetics by Heidner and coworkers4 and by Lilenfeld5 postulated that vibrationally excited iodine was a likely energy carrier in a multistep dissociation process. Hall et al.6 demonstrated the \( ^1S+I \) reaction rapidly produces \( I_2(x,v \leq 43) \) and Davis and Van Benthem7 observed \( I_2(x,v) \) in a flow of \( O_2(a,b) \) and \( I_2 \). However, recent detailed investigations by Heaven et al.8 of collisional energy transfer among \( I_2(X,v) \) levels indicates that vibrationally excited \( I_2 \) may not be the energy reservoir needed for rapid \( I_2 \) dissociation. To assist in unraveling the dissociation mystery and to help COIL developers better understand the operation of devices, we have also recently developed a sensitive diagnostic for the \( I_2 \) dissociation fraction within the COIL cavity.9,10 This device will be important to assess the mixing efficiency of \( I_2 \) with the primary singlet oxygen flow.

The combination of the potential for COIL as an efficient, high power laser with good beam quality and the unanswered scientific questions about its operation have led to the development of several sensitive diagnostics that are now

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providing critical insight into this important and scientifically interesting laser system. In this paper we discuss several
diagnostics that we have been developing that provide researchers with monitors for several important species and
parameters including:

- Small signal gain
- Water vapor concentration
- Singlet oxygen yield
- Translational temperature
- I$_2$ dissociation fraction
- Mixing uniformity.

We also preview some new diagnostics that will provide COIL researchers with additional diagnostic capabilities for
emerging and future iodine lasers.

2. ESTABLISHED COIL DIAGNOSTICS

Chemiluminescence methods were among the first diagnostics for COIL and were skillfully applied by Derwent and
Thrush$^{2,3}$ in their pioneering work that led to the prediction that a COIL could be developed. Later, chemiluminescence
methods were used to monitor the number densities of both O$_2$(a) and FP$_{1/2}$ in early laser development research.
Indeed, the first successful COIL demonstration used the ratio of the chemiluminescence intensity emitted along the
optical axis to that emitted from the side as a monitor for axial stimulated emission, and this led to optimization of
conditions for laser oscillation.$^1$

COIL has been existence for over 25 years, and consequently has benefited from the development of advanced photonic
laser sources and detectors during this time. Indeed, the development of single frequency, fiber coupled, tunable diode
lasers during this time has been dramatic. We have taken advantage of these devices and applied them directly to
COIL. In the following sections we briefly describe some of these systems and provide some of the sensitivities and
capabilities of these systems. Since we have discussed many of these systems previously,$^{11,12}$ we only provide a brief
discussion.

2.1. Small signal gain

The stimulated emission cross section for the COIL laser transi-
tion is only ~ 7.5x10^{-18} cm$^2$ at room temperature, and the upper
state number density is typically ~ 10^{15} cm$^{-3}$. Consequently, the
optical gain is relatively low and an accurate small signal gain
(SSG) diagnostic is a valuable tool, not only for developing a
COIL device, but also for gaining a better understanding of its
operation. Phenomena that reduce or increase the SSG are
extremely important to identify and characterize.

We have developed and refined an ultra-sensitive diode laser
based monitor for the atomic iodine 2P$_{1/2}$ - 2P$_{3/2}$ transition including
all six hyperfine components.$^{11,12}$ An absorption spectrum that covers all six hyperfine components is shown in
Fig. 1. For many applications, the small signal gain is a key parameter. For example, several research groups$^{13-15}$ have
used fiber optic coupled, IodineScan systems to measure small signal gain profiles on existing COIL systems to assess
performance and to compare to analytical predictions. Spatial profiles of the small signal gain provide key insight into
iodine injector performance. These diagnostics have also recently been used to guide the development of new iodine
lasers. The All Gas Iodine Laser (AGIL), an important new chemical iodine laser was developed using a diode laser
small signal gain diagnostic to optimize conditions for laser oscillation.$^{16}$ As we discuss below, the IodineScan gain
diagnostic is also being applied to emerging laser systems such as the discharge oxygen iodine laser (DOIL).

2.2. Water vapor

Using a diode laser that operates on the strong water vapor absorption line near 1.39 µm, we also have developed a
small, sensitive system for water vapor that is now used routinely to assess the performance of chemical singlet oxygen
generators and to monitor the water vapor present in the cavity. One important piece of information provided by these
sensors, especially for rotating disk generators, was the rather rapid increase in the water vapor pressure in the cavity as the chemical generator produced waste heat.

2.3. Singlet oxygen yield
We use a 0.76 µm diode laser to probe the O₂(b – X) system as a quantitative measure of the ground state oxygen produced by the chemical generator.¹¹ Assuming that each Cl₂ molecule introduced into the chemical generator produces one oxygen molecule (regardless of electronic state) the Cl₂ mass flow valve can be combined with the measurement of the ground state number density O₂ (measured with the diode laser) to infer the number density of O₂(a) in the cavity. This method has been successfully applied to a variety of singlet oxygen generators (SOGs) including both disk and jet generators. One can also infer “n”, the number of singlet oxygen molecules consumed in dissociating the molecular iodine.

In addition to standard chemiluminescence methods for determining singlet oxygen yield, several other methods have been described in the literature. Lilienfeld⁵ used Electron Spin Resonance (ESR) to determine the yield of both a microwave source and a chemical generator. While quite accurate, ESR is not a practical diagnostic for COIL. Gylys and Rubin¹⁷ used pulsed Raman Scattering to determine the populations of both O₂(a) and O₂(X) in a chemical generator, and this method is also being further developed. Most recently, Williams and coworkers¹⁸ have used intracavity methods and a diode laser to measure the absorption spectrum of the molecular oxygen Noxon bands (O₂(b) ← O₂(a)). The absorption linestrength of this transition has not been measured, but has been calculated.¹⁸ This method may also hold promise as an alternate singlet oxygen diagnostic.

2.4. Temperature measurements
Since we scan complete absorption line profiles with the diode laser, we can infer the translational temperature by determining the Doppler profile of the measured absorption curve. To obtain the most accurate temperature measurements one must extract the Gaussian component of the lineshape from the Voigt profile that also contains the collisionally broadened (Lorentzian) component of the lineshape. We have previously published linebroadening coefficients for most of the major components in COIL systems for all three sensors: oxygen,¹⁹ water vapor,¹⁹ and atomic iodine.²⁰, ²¹ Consequently, one can use the recorded lineshapes to determine the translational temperature in either the SOG or the laser cavity.

3. NEW AND EMERGING DIAGNOSTICS FOR COIL

3.1. Two dimensional imaging
Until now we have discussed point, line of sight measurements for species concentration, temperature, and singlet oxygen yield. As mentioned above, several research teams have used the iodine atom sensors to spatially map the small signal gain and temperature the cavity by scanning the collimated diode laser beam across a selected volume within the resonator. This has provided detailed information concerning the mixing of the iodine into the singlet oxygen primary flow and has helped researchers to develop more efficient COIL devices. While these spatial scans provide valuable data, they require tens of seconds to record even a 1-D line of information. To record a series of lines to map out 2-D features requires considerably more time, and the conditions may change.

Recently, we have begun development of new diagnostics that will facilitate full, nearly instantaneous 2-D imaging of reactive flowfields within COIL. We have coupled a PSI diode laser diagnostic to a 2-D InGaAs array camera. This imaging configuration permits over 81,000 simultaneous points in the flow to be interrogated simultaneously. For these initial measurements we used a WaterScan diagnostic to probe water vapor in a flow at 1.39. However, the same technology will be applicable to I atoms. We used a simple telescope to expand the beam exiting the fiber optic of the WaterScan diode laser. The expanded beam was detected by a 256x380 InGaAs array camera. We developed several software routines to both scan the diode laser and to efficiently reduce the data from all pixels. The apparatus is shown in Fig. 2.

To test this system we first injected a known amount of water vapor through the 5.5 cm diameter flow reactor with the injector far upstream of the observation point. Thus, the concentration of the water vapor in the flow reactor at the positions of the expanded diode laser beam was uniform under these conditions. This allowed us to test the quantitativeness of the imaging diagnostic.
In Fig. 3 we show a curve of growth for the absorbance measured from a single pixel as a function of water vapor in the flow reactor. The slope gives a linestrength of $1.23 \times 10^{-20}$ cm$^{-1}$/cm$^2$-molecule in excellent agreement with the literature value of $1.24 \times 10^{-20}$ cm$^{-1}$/cm$^2$-molecule. The linearity of the data and the agreement with the literature value imply that the individual pixel data provide an accurate measurement of the water number density.

We also developed software to automatically scan the diode laser in steps over the entire water vapor absorption line. In Fig. 4 we show a typical absorption lineshape trace of 100 data points (each representing a different diode laser wavelength as the water line was scanned). These data were from a single pixel. Also shown is a Voigt fit to the data. Analysis of the Voigt fit produced a translational temperature of 288K, consistent with experimental conditions and demonstrated the quantitiveness of the diagnostic.

In Fig. 5 we show an image of the water vapor concentration exiting a small 1 mm high nozzle. For these measurements we inserted the small nozzle within the viewing area of the imaging diode laser diagnostic. The nozzle exit is on the left hand side of the figure and the water vapor plume obvious. We plan to extend this diagnostic to atomic iodine in the near future. We expect that we will be able to obtain full field imaging of the small signal gain spatial profiles and images of the spatial profile of the translational temperature. While this diagnostic is in its early stage of development, it has the potential for providing data of unprecedented detail including mixing and the uniformity of the small signal gain and temperature within the cavity of COIL devices. This will be valuable in assessing new mixing schemes and injectors.

### 3.2. Molecular iodine dissociation fraction

As mentioned previously, the dissociation of molecular iodine is one of the remaining unresolved issues in COIL kinetics. It is important not only from a basic science perspective, but the dissociation also removes singlet oxygen from the flow that would otherwise be available as extractable output power. It is generally accepted that from 4-6 singlet oxygen molecules are required to dissociate one iodine molecule. Endo and coworkers$^{22}$ have used microwave discharges of I$_2$ prior to injecting into the primary flow to “pre”-dissociate the iodine. However, recombination of some of the iodine has limited this method.

Various mixing schemes for injecting molecular iodine into the primary flow have also been developed and tested in COIL devices including injection into the subsonic, transonic, and supersonic regions of the flow. Knowledge of the
dissociation spatial profile would provide valuable insight into injector location and operating conditions. Clearly, if the I₂ is not uniformly mixed into singlet oxygen flow, dissociation will be relatively slow and inefficient. This will be particularly true for some of the newer nozzle and injector concepts.

We have recently developed a prototype sensor to monitor I₂ dissociation in the cavity of COIL that is independent of temperature and simple to use. This diagnostic is based on our earlier sensor for I₂ mass flow. We use 488 nm light to probe the continuum absorption in I₂. The cross section is well established, \( \sigma_{\lambda} = 488\text{nm} = 1.64 \times 10^{-18}\text{cm}^{-2} \) and since the absorption from the ground \( X^1\Sigma^+ \) state terminates on a continuum state, the absorption is essentially independent of the Boltzmann temperature of the ground state for COIL conditions. We have combined an intense light emitting diode (LED) with a Si detector to form an ultra-sensitive detection system. The heart of the sensor is a circuit that provides 20 bit resolution and allows us to detect absorptions as small as 1 part in \( 10^6 \). In a small flowtube reactor we have measured \([I₂] \sim 5 \times 10^{11}\) in a 5.6 cm path. Since COIL usually uses initial \([I₂] \sim 10^{15}\ \text{cm}^{-3}\), this implies that we should be able to detect dissociations of greater than 99%. Plans are underway to complete measurements on a COIL device.

3.3. Singlet oxygen yield

The yield of singlet oxygen is one of the most important parameters in COIL devices, and accurate determinations of the yield can be used to assess the overall chemical efficiency and extraction efficiency of a device. We mentioned previously that chemiluminescence, ESR, and diode lasers have been used to determine the yields. Absolute chemiluminescence is usually considered to be uncertain by at least 20% because of the difficulties in calibrating the detection system for volumetric observations. ESR is not practical for an operational COIL device.

We have combined the I₂ diagnostic with the IodineScan diode laser system to develop a new diagnostic for the singlet oxygen yield that depends only on the strong equilibrium established between four species: \([I], [I^*], [O₂(X)], \) and \([O₂(a)], \) in COIL. The equilibrium constant, \( K_{\text{eq}} \) is given by Eq. (1).

\[
K_{\text{eq}} = [I^*][O₂(X)]/[I][O₂(a)].
\]

Rewriting we find:

\[
[O₂(a)]/[O₂(X)] = K_{\text{eq}}[I^*]/[I].
\]

The I₂ monitor provides a measure of the quantity \([I] + [I^*]\) if measurements are taken with and without O₂(a) present in the flow. The diode laser diagnostic provides \([I^*] - [I]/2\). We can use these two measurements to determine the ratio \([I^*]/[I]\). In addition the Gaussian component of the iodine atom absorption lineshape measured by the diode laser sensor gives the temperature from which \( K_{\text{eq}} \) can be determined. As shown explicitly in Eq. (2), these measurements determine the ratio \([O₂(a)]/[O₂(X)]\) from which we can infer the yield, defined as \( Y = [O₂(a)]/[O₂(a)] + [O₂(X)]\).

We have used this method to measure the O₂(a) yield produced by a microwave discharge of oxygen, and present the yield as a function of microwave discharge power in Fig. 6. Details are provided in references 9 and 10. We will soon repeat these measurements for a chemical generator.

3.4. Application of diagnostics to DOIL and AGIL

There has been renewed interest recently in developing an oxygen iodine laser based on electric discharge production of singlet oxygen. In the past few years there have been reports of singlet oxygen yields greater than 20% and even laser oscillation on the iodine atom. These laser reports have been retracted, but the interest in developing a DOIL remains high.

Very recently, Carroll et al. at the University of Illinois have reported positive gain on a DOIL system with the singlet oxygen produced by an r-f discharge. This system produced singlet oxygen yields of about 15%, and they used a supersonic expansion to cool the translational temperature to about 200 K. They used the equilibrium method just described to estimate the singlet oxygen yield and an IodineScan diode laser to probe for gain and temperature in the flow to optimize conditions and indeed were able to measure positive gain for this system as reported in this conference.

![Fig. 6. Singlet oxygen yield measured using equilibrium method. Excited oxygen produced by a microwave discharge.](image-url)
In a complementary set of experiments, Rawlins et al.\textsuperscript{25} used a low power (70W) Evenson cavity microwave discharge to produce singlet oxygen yields of approximately 25\% in dilute (5\% oxygen in argon) discharges. We used an ultrasensitive version of the IodineScan system to measure positive gain in a room temperature (340 K) flow. These two experimental results provide important data that a DOIL system can indeed be demonstrated.

We discussed above how a diode laser sensor for small signal gain played an essential role in the successful development of AGIL. This iodine laser uses NCl(a) in place of O$_2$(a) as the energy transfer partner. In this system, Manke\textsuperscript{16,26} et al. have used hydrogen azide based chemistry to produce the NCl(a). Coombe\textsuperscript{27} developed an alternate chemistry based on amine reactions to produce NCl(a):

\[
\text{NCl}_3 + H \rightarrow \text{NCl}_2 + \text{HCl}
\]
\[
\text{NCl}_2 + H \rightarrow \text{NCl}(a) + \text{HCl}
\]

Two groups led by McDermott\textsuperscript{28} and Hunter\textsuperscript{29} are investigating this chemistry as a possible source for an AGIL device. Preliminary results from Hunter are shown in Fig. 7. An IodineScan diagnostic was used to probe iodine atoms that were injected into a flow of NCl(a). The data clearly indicate chemical pumping of the I atom manifold in the presence of NCl(a). We are reconfiguring our system and will attempt to measure positive small signal gain.

4. SUMMARY

In this brief survey we have provided a short history of important diagnostics for COIL. These include both passive and active optical diagnostics. Diode laser sensors have become standards for characterizing existing COIL systems and are valuable tools both for understanding scientific issues with COIL and for testing new concepts such as scaling. We also presented several new diagnostic approaches that we have been recently developing. These will provide further insight into COIL kinetics and mixing. We also have described how some of these diagnostics have helped to establish new and potentially important iodine laser systems such as AGIL and DOIL.

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