

UNCLASSIFIED

Defense Technical Information Center
Compilation Part Notice

ADP012382

TITLE: Historical Perspective of COIL Diagnostics

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Gas and Chemical Lasers and Intense Beam Applications III Held
in San Jose, CA, USA on 22-24 January 2002

To order the complete compilation report, use: ADA403173

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:

ADP012376 thru ADP012405

UNCLASSIFIED

Historical perspective of COIL diagnostics

Steven J. Davis*
Physical Sciences Inc.

ABSTRACT

In this paper, I present a history of the development of diagnostic techniques for the chemical oxygen iodine laser (COIL). Several established optically based techniques have been applied to COIL including: visible and near infrared chemiluminescence, resonance absorption, and laser induced fluorescence. I trace the history of these developments using the diagnostic methods as the overall theme. In many cases a variant of an established diagnostic was used to probe for some key kinetic rate or mechanism. Indeed, the goal of developing the now well established COIL kinetic rate package was responsible for the introduction of new diagnostic methods. I discuss diagnostics both before and after the demonstration of the first COIL device.

Keywords: Chemical Oxygen Iodine Laser, optical diagnostics, development history

1. INTRODUCTION

During this commemorative session on the 25th anniversary of the invention of COIL, we are recounting the history of the development of this unique laser system.¹⁻³ The excellent reviews of the laser development and COIL kinetics by Bill McDermott⁴ and Mike Heaven⁵ earlier in this volume provide ample motivation for a discussion of diagnostics.

In the following pages I have described some of the developments that led to the present diagnostic toolbox now available to COIL researchers. Before launching into a detailed discussion of COIL diagnostics it is important to at least mention the important species and parameters relevant to COIL development. I will be brief here since others have already covered much of this earlier in these proceedings.

Although numerous diagnostic methods have been developed and applied to COIL, it is important to emphasize that this has not been an isolated journey. In many cases, some kinetic rate or elucidation of a reactive mechanism was needed. This led either to a variation of an existing diagnostic or the development of a new method. Most frequently it was the former, and this is entirely reasonable; application of a well-proven technique to a new problem is often a prudent approach.

In this brief overview, I will attempt to trace the highlights of COIL diagnostic development. I have been privileged to be part of this area during and after the demonstration of the first COIL. While I have tried to provide a historical background, the reader will note that my review is not entirely chronological. Rather, I chose to frame the review around several general, optical and even non-optical techniques. I hope that this does not trouble the reader, but it is how I mentally categorized the history of COIL diagnostics.

There now exists a fairly extensive toolbox of diagnostics available to the COIL developer, and these are listed in Table 1. In the following survey, I will highlight the development of several of these "tools".

* sdavis@psicorp.com; phone 1 978 689 0003; fax 1 978 689 3232; <http://www.psicorp.com>; Physical Sciences Inc.,
20 New England Business Center, Andover, MA, USA 01810-1077

Table 1. "Toolbox" of diagnostics that have been applied to COIL

Method	Species/Parameter	Method	Species/Parameter
• Near-IR chemiluminescence	$\left\{ \begin{array}{l} \text{O}_2(a^1\Delta) \\ \text{I}({}^2\text{P}_{1/2}) \\ \text{I}_2(\text{A}^3\Pi_1) \end{array} \right\}$	• Laser-induced fluorescence	$\left\{ \begin{array}{l} \text{Mixing} \\ \text{Reaction layers} \end{array} \right\}$
• Visible chemiluminescence	$\left\{ \begin{array}{l} \text{O}_2(b^1\Sigma) \\ \text{I}_2(\text{B}^3\Pi_0) \\ \text{O}_4^* \\ \text{Temperature} \end{array} \right\}$	• Raman spectroscopy	O ₂ * yield
• Electron spin resonance	$\left\{ \begin{array}{l} \text{O}_2(\text{X}^3\Sigma) \\ \text{O}_2(a^1\Delta) \\ \text{I}({}^2\text{P}_{3/2}, {}^2\text{P}_{1/2}) \end{array} \right\}$	• Pressure meters	Species concentration
• Resonance absorption	$\left\{ \begin{array}{l} \text{I}({}^2\text{P}_{3/2}, {}^2\text{P}_{1/2}) \text{ (gain)} \\ \text{O}_2(\text{X}^3\Sigma) \text{ (yield)} \\ \text{H}_2\text{O} \\ \text{Temperature} \\ \text{I}_2 \text{ mass flow} \\ \text{I}_2 \text{ dissociation} \\ \text{Cl}_2 \text{ mass flow} \end{array} \right\}$	• Mass flow meters	"Fuel" flows
		• Power meters	Laser output power

The history of when these various diagnostic tools were developed and/or applied to COIL related research is summarized in Fig. 1. This figure is only intended to be a rough guide.

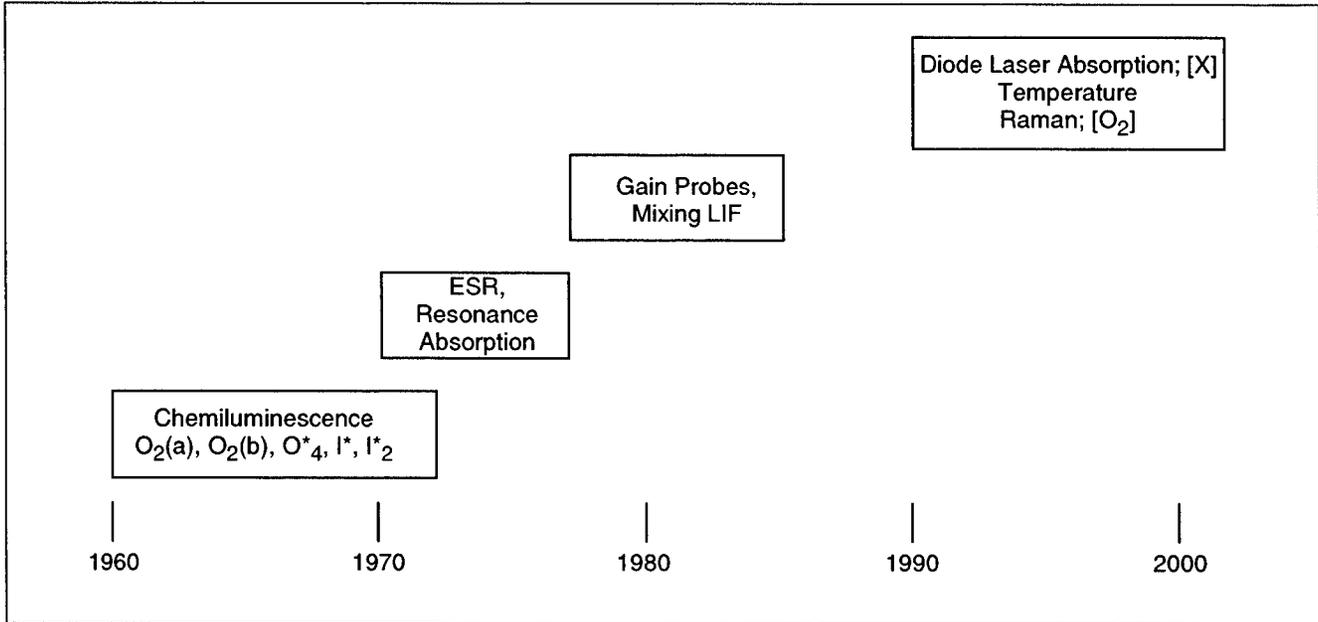
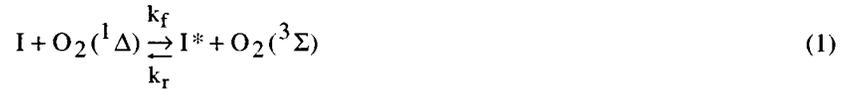


Fig. 1: History of COIL diagnostic development.

The overall COIL kinetics are well documented and we only present the essential features here. In brief, the system is described by Eqs. (1) through (3).



The equilibrium condition for inversion of the atomic iodine in COIL is given by Eq. (4)

$$K_{eq} = \frac{k_f}{k_r} = 0.75 \exp(402/T) \quad (4)$$

At room temperature, the atomic iodine lasant species can be inverted with about 18% of the oxygen in the O₂(¹Δ) state. The fraction of the oxygen required to invert the iodine is less at lower temperatures. This means that any additional singlet delta oxygen can be used to derive output power from the COIL device.

The reader will note that I have neglected the dissociation process in the reactions listed above. This was discussed in detail in Mike Heaven's paper earlier in this volume.⁵ From the above, we can deduce that knowledge of the concentrations of O₂(¹Δ), O₂(³Σ), I(²P_{1/2}), I(²P_{3/2}), and temperature are crucial. In addition, monitors for O₂(¹Σ) and H₂O were target species early in COIL development because of their potential roles in the molecular iodine dissociation. Water vapor is a known quencher of the upper laser level I(²P_{1/2}) in COIL.

2. EARLY DEVELOPMENTS

2.1 Chemiluminescence

Chemiluminescence often provides a convenient method for tracking excited state species, but it provides no information on the ground states of the relevant emitters since only spontaneous emission is observed. Knowledge of excited state lifetimes can in principle be used to determine the concentrations of the emitting states. However, calibration of the detection system and taking proper account of the viewing geometry often introduce considerable error into the chemiluminescence method. In general, determination of excited state species by absolute chemiluminescence methods is accurate to only about $\pm 40\%$. In spite of these issues, chemiluminescence is often the most sensitive and efficient diagnostic tool for initial assessment of a candidate chemical laser system.

Elmer Ogyzlo et al.⁶ used chemiluminescence to monitor $O_2(^1\Delta)$, $O_2(^1\Delta)_2$, $I(^2P_{1/2})$ and $O_2(^1\Sigma)$. Indeed, in this strikingly brief, yet succinct paper, they described several of the key issues related to COIL. These include energy transfer from $O_2(^1\Delta)$ to I atoms, energy probing of two $O_2(^1\Delta)$ molecules, and ominous comments about the still not completely understood I_2 dissociation mechanism.

Derwent and Thursh⁷⁻⁹ also used chemiluminescence to probe the products of the interaction of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ with I_2 . In a series of seminal papers they described the results of several key experiments. For example, in Fig. 2 we show the vibrational distribution in $I_2B(^3\Pi)$ produced in the interaction of both $O_2(^1\Sigma, ^1\Delta)$ with I_2 .

They used these and similar data to suggest kinetic mechanisms, and some of these ideas are still valid. By using chemiluminescence to derive populations of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$, and establishing the equilibrium constant, they predicted that an atomic iodine laser pumped by $O_2(^1\Delta)$ would be possible.

2.2 Resonance absorption and fluorescence

The atomic structure of the lower levels of atomic iodine are not only favorable for laser oscillation but are also readily probed via strong optical transitions in the UV region. In Fig. 3 we show the spin orbit terms ($^2P_{3/2}$) and ($^2P_{1/2}$) of the groundstate $5s^2p$ configuration. Since these two states arise from the same configuration, the $^2P_{1/2}$ level is metastable with respect to $^2P_{3/2}$ via LaPorte's rule.

In contrast (as shown in Fig. 3), the strong, radiatively allowed transition to the analogous state of the $5p^46s$ configuration provides sensitive probes for the $^2P_{1/2,3/2}$ states. Husain and coworkers^{10,11} took full advantage of this and reported a long series of kinetic measurements of the $^2P_{1/2}$ state. This early work provided not only important kinetic rate coefficients and estimates of the radiative lifetime of the $^2P_{1/2}$ state, but also laid the foundation for a diagnostic crucial to COIL.

2.3 The first gain measurement

Dave Benard led a group from the Air Force Weapons Laboratory (AFWL), the Rockwell Science Center and Rocketdyne Inc. in a key demonstration experiment.¹² The setup is shown in Fig. 4. Rocketdyne had developed a singlet oxygen generator using the reaction of chlorofluorosulfate (CFS) with H_2O_2 and had measured singlet oxygen yields of 35%.

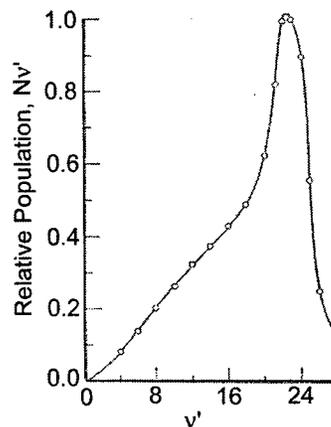


Fig. 2: Vibrational distribution within $I_2(B)$ produced by singlet oxygen pumping and obtained by Derwent and Thrush from visible chemiluminescence.

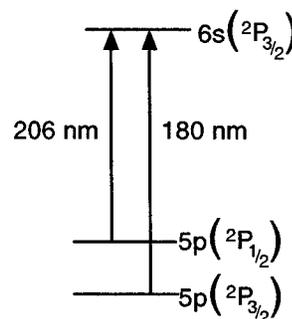


Fig. 3: Low lying energy levels of atomic iodine.

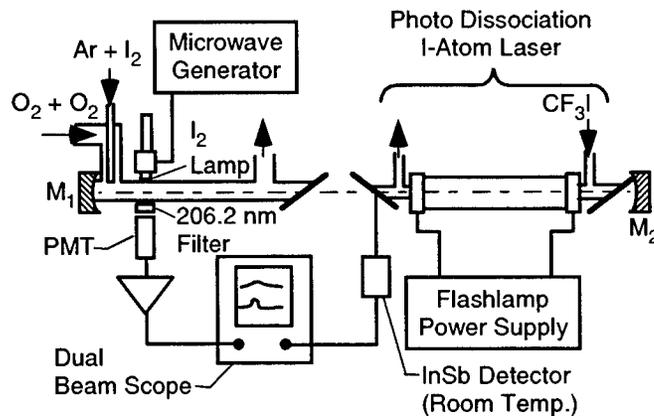


Fig. 4: Experimental arrangement for the first gain measurement in COIL.

The idea behind the diagnostic was to saturate the $I(^2P_{1/2} \leftarrow ^2P_{3/2})$ transition with a strong pulse from an I atom photolysis laser. If the $^2P_{1/2}$ state is inverted with respect to the $^2P_{3/2}$ then the saturation pulse will drive population down from the $^2P_{1/2}$ state to the $^2P_{3/2}$ state. The relative population of the $^2P_{1/2}$ and $^2P_{3/2}$ states was monitored with a resonance lamp operating at 206 nm (see Fig. 4). Using this sensitive double resonance approach, Benard and coworkers¹² were able to demonstrate weak, but certain positive gain in a singlet oxygen pumped iodine atom flow system. This provided the crucial data needed to maintain the focus and the program to produce a chemically pumped short wavelength laser.

2.4 "First light"

Recognition of the fundamental differences in the spatial and directional distributions between spontaneous and stimulated emission led to the key optical diagnostic that guided the first successful COIL laser demonstration. The basic idea is shown in Fig. 5. Two Ge detectors were positioned next to the longitudinal flow cavity region. Detector A probed along the optical axis and detector B examined the light emitted normal to the optical axis. Consequently, detector A was sensitive to stimulated emission directed along the resonator axis, and detector B detected spontaneous emission emitted normal to the optical axis. The approach to laser oscillation in any laser includes a buildup of stimulated emission intensity along the resonator axis. Thus one expects that the end detector A will show a faster rise than the side viewing detector B. This is exactly what was seen on the first COIL. The end detector initially became noisier than the side detector as the intensity along the optical axis grew due to stimulated emission. Finally, as laser threshold was reached, the end detector "pegged." A power meter showed 4 mW output. Transverse mode structure was observed on an IR sensitive card, confirming laser oscillation.¹

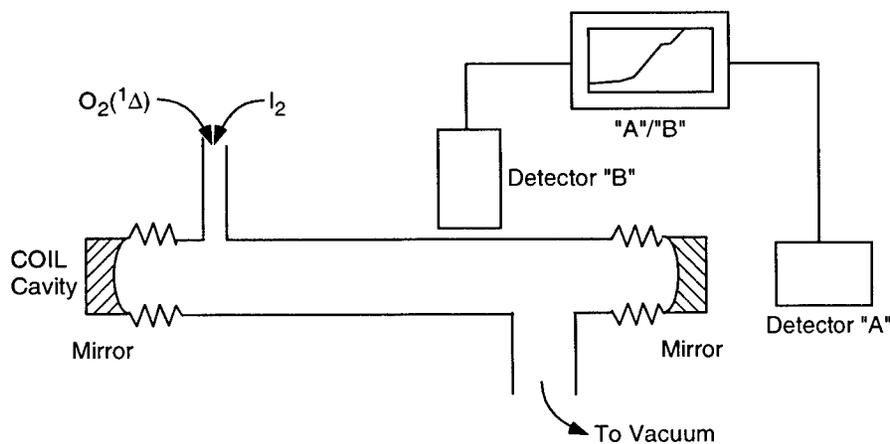


Fig. 5: Experimental arrangement for the first COIL gain measurement.

3. POST LASER DEMONSTRATION DIAGNOSTICS

3.1 Introduction

The laser demonstration¹ of 1 December 1977 was a defining moment in the history of COIL diagnostics. In general, the diagnostics prior to December 1, 1977 were developed to support this key milestone. Subsequent to the laser event, it was clear that the COIL kinetic mechanisms and rates needed serious development. This led to a renaissance of kinetics studies that has not been equaled since that time. Premier federal, industrial, and academic laboratories were focused on this system for a period of about 5 years.

3.2 Chemiluminescence

Soon after the first demonstration of COIL, the group at Aerospace Corp headed by Rick Heidner began a systematic and detailed series of experiments to determine key kinetic mechanisms and rate coefficients.^{13,14} Using a microwave source for excited oxygen and a temperature controlled flow reactor, they produced kinetic data that are used to this day. From these data they developed possible mechanisms for the molecular iodine dissociation that were discussed earlier by Mike Heaven.⁵ These data have withstood the test of time for nearly two decades and comparisons continue to be made between new models for the dissociation to the data-base produced by this excellent work.

At AFWL (now the Air Force Research Laboratory), my research group was involved with an active program to examine candidates for short wavelength chemical lasers. We were already involved in developing diagnostics for COIL. These diagnostics included both passive (chemiluminescence) and active (resonance absorption and fluorescence) techniques. Before describing some of the active techniques, I want to discuss some of the interesting results that we obtained from the chemiluminescence work.

The dissociation of molecular iodine had been an elusive problem for many years. Using a small flow tube and a microwave discharge to produce singlet oxygen, we made some initial probes into the efficiency of the dissociation process by monitoring the number of singlet oxygen molecules consumed to dissociate one iodine molecule.¹⁵ The experiment was relatively simple: measure the consumption of singlet oxygen as a function of the added I₂. We used an optically based mass flow meter to measure the iodine mass flow. In Fig. 6 we show results from that experiment that imply that the dissociation efficiency increased as the molecular iodine was increased. While not defining a mechanism or producing kinetic rates, this early experiment did imply that iodine itself might be active in the dissociation process.

We also developed a Fabry-Perot interferometer to examine the collisional broadening of the hyperfine components of the I (²P_{1/2} → ²P_{3/2}) transition, again using chemiluminescence.¹⁶ A microwave production source produced O₂(¹Δ), and this flow was added to a small flow tube reactor that also mixed in I₂. We spectroscopically examined the hyperfine components of the atomic iodine chemiluminescence emission as shown in Fig. 7.

Examination of these spectra as a function of added oxygen yielded the first broadening data under COIL conditions and demonstrated that the prior concerns about an anomalously large oxygen broadening of the COIL laser transition were unfounded. We concluded that under COIL conditions, the reduction in the line center gain on the (3,4) transition caused by oxygen collisional broadening would be minimal.

There are several possible methods for determining the flow temperature. Thermocouples can be used, but the metastable oxygen leads to errors in thermocouple measurements due to deactivation of the excited oxygen on the thermocouples. In addition, thermocouple measurements are notoriously inaccurate in rarified, supersonic gas flows

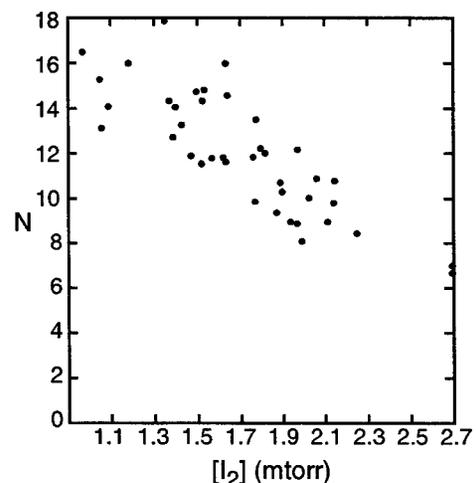


Fig 6: Plot of the number of singlet oxygen molecules required to dissociate an I₂ as a function of the I₂ concentration.

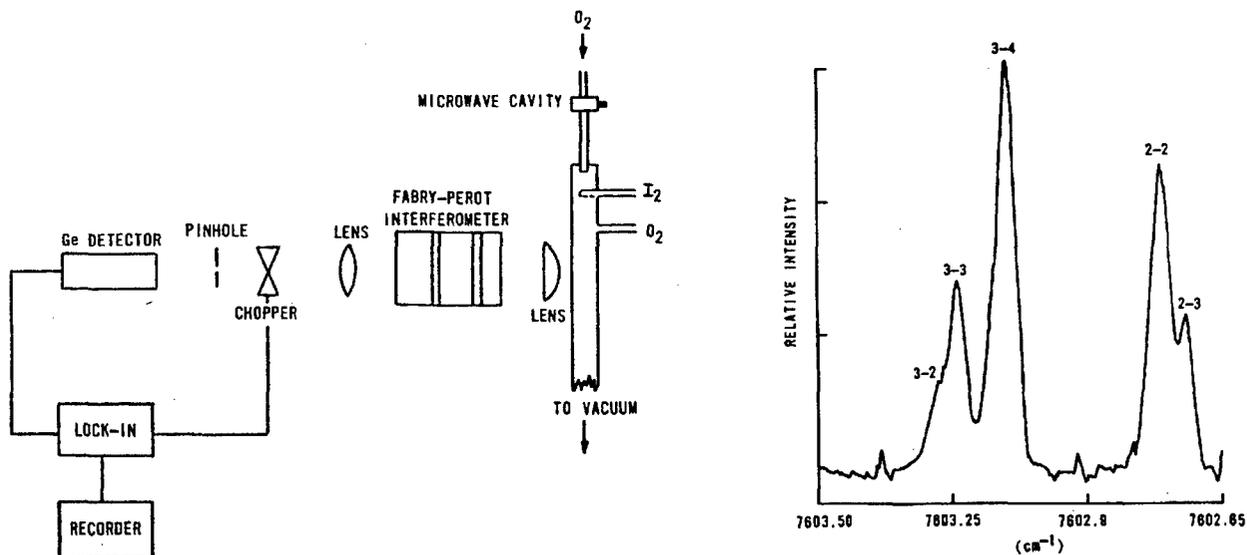


Fig. 7: Partially resolved hyperfine structure from atomic iodine produced by the interaction of molecular iodine with singlet oxygen and recorded with a Fabry-Perot interferometer.

such as in COIL. Other potential methods include measurement of the rotational temperature of species in the flow such as the rotational manifold of oxygen. Van Benthem and Davis¹⁷ demonstrated a variant of this approach by monitoring the rotationally resolved emission on the $O_2(b \rightarrow X)$ system produced in chemical oxygen generators used in COIL. We determined the temperature $T = 310$ K over a large sparger singlet oxygen generator on the AFWL COIL IV. While potentially useful, one must be assured that the rotational manifold of the electronically excited $O_2(b)$ state is at the translational flow temperature, and this may not be true at typical low pressure COIL conditions.

3.3 Resonance absorption

Most "active" diagnostics developed for COIL during this period used resonance absorption and fluorescence. Interestingly, several diagnostics that we developed used the optical ($B \leftarrow X$) transition in I_2 . Indeed, at least four diagnostics were based on this absorption band:

- I atom probe laser
- I_2 dissociation fraction
- I_2 mass flow meter
- Laser induced fluorescence for flow mixing.

The relevant energy levels of the $I_2(B-X)$ system are shown in Fig. 8. The B state correlates to one excited and one ground state atom. For excitation wavelengths longer than about 501 nm, strong, visible fluorescence is produced. In contrast, when excited by optical wavelengths less than 500 nm, the visible fluorescence is dramatically reduced. However, strong emission from the excited $I(^2P_{1/2})$ is produced. We used this selective process to produce the first I atom laser based upon photolysis of I_2 .¹⁸ This has distinct advantages over photolysis of alkyl-iodides such as CF_3I , because I_2 regenerates itself from I atom recombination. We used this simple, dye laser pumped I atom laser to probe for gain on COIL IV, and it identified a chemically induced coating problem on the COIL cavity mirrors.

Len Hanco and I developed an iodine mass flow meter based on the continuum absorption near 490 nm from the ground state of I_2 .¹⁹ The concentration of molecular iodine in a cell can be determined directly from such a measurement. If the cell is in line with the iodine delivery system in a COIL, then one can use this approach to determine the mass flow of the iodine. One needs to measure the mass flow rate and pressure of the carrier gas in the same cell, but these parameters can be readily measured with a mass flow meter and capacitance manometer respectively.

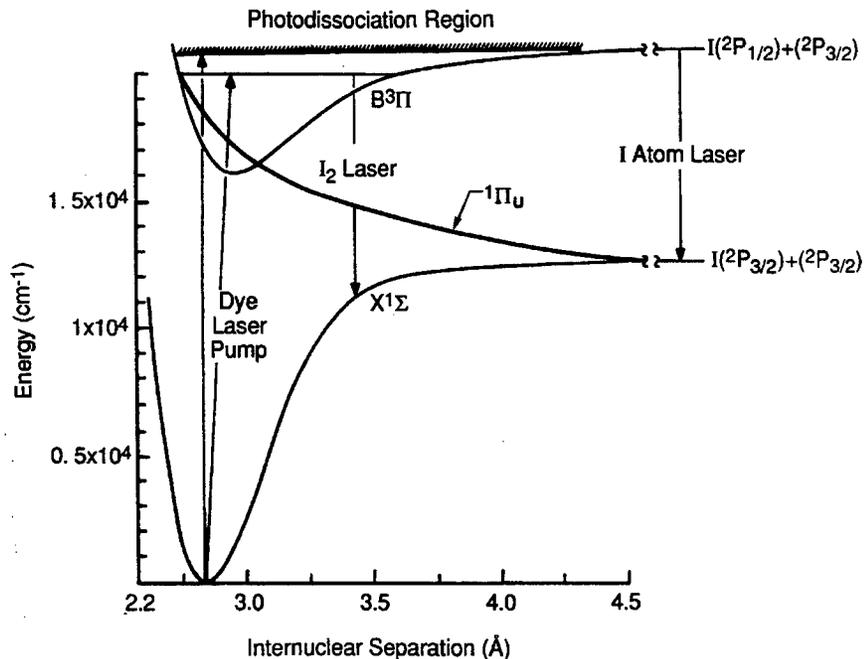


Fig. 8: Energy levels in I₂ relevant to several COIL diagnostics.

Iodine dissociation fraction measurements in the cavity of COIL devices are made using an analogous strategy. One monitors the absorption on a bound-bound transition of the B-X system. As the iodine is dissociated, the absorption is reduced, and this provides a direct measurement of the dissociation fraction.

Hall, Marinelli, and Houston²⁰ completed an important experiment in 1983 that conclusively demonstrated that highly vibrationally excited I₂ was a major product of the quenching of I(2P_{1/2}) by molecular iodine. They detected I₂(X; 25 ≤ v' ≤ 43) using laser induced fluorescence to probe the products of this quenching process. Following up on this excellent work, we used laser induced fluorescence to probe the dissociation region in a flow of singlet oxygen and molecular iodine and observed a similar distribution of vibrationally hot ground state I₂.²¹ This combined with the prior chemiluminescence results of Heidner,^{13,14} Lilienfeld,^{22,23} and Alsing,¹⁷ confirmed that iodine was an active participant in its own dissociation.

Finally, with respect to visible wavelength resonant absorption techniques, I should mention the flow field visualization that Larry Rapagnani and I developed for studying mixing in subsonic and supersonic chemical laser flow fields.²⁴ We injected iodine vapor into the plenum of a cw, HF chemical laser run without fuels. The nozzle was a CL II supersonic device. We used an argon ion laser operating at 514.5 nm to excite the v'=43 level in I₂(B) at several selected locations downstream of the nozzle. A photograph of the planar laser induced fluorescence emitted by the excited iodine molecules is shown in Fig. 9. The LIF originates from the argon ion laser beam slightly downstream of the nozzle exit bank and persists for about 2 cm, consistent with the Mach 3 flow and the radiative lifetime of the I₂(B) excited state. With the advent of CCD cameras, this method progressed from a qualitative demonstration to a quantitative technique to study mixing in chemical lasers. Numerous COIL development facilities have used this LIF technique to assess mixing in advanced nozzles.

3.4 Electron paramagnetic resonance

The group at MDRL led by Harvy Lilienfeld completed a comprehensive series of kinetics measurements that used chemiluminescence, EPR, spectroscopy, and LIF.^{22,23,25} They used these tools to excellent advantage and produced a series of reliable and important kinetics rates, many of which are now in the Air Force standard rate package for COIL. They also made significant contributions to the understanding of important kinetic mechanisms including the dissociation process.



Fig. 9: LIF image of nozzle effluent pattern in a Mach 3 chemical laser flowfield. The image is from laser excited molecular iodine. Flow is down in the picture.

3.5 Diode laser sensors

With the advent of reliable, near IR laser diodes, a new class of diagnostics based on resonance absorption became feasible. The telecommunications industry was the main catalyst for the development of these new lasers that are now used as sources for wavelength division multiplexing (WDM) and dense wavelength division multiplexing (DWDM) applications. Low loss and low dispersion fiber optics in the 1.3 to 1.65 μm spectral region led to the development of superior lasers in this spectral window for telecommunications. Narrow and controllable wavelengths from the diode lasers is crucial for DWDM, and distributed feedback (DFB) lasers were developed for this purpose. At Physical Sciences Inc. (PSI) we recognized that this could lead to a new class of sensitive diagnostics for COIL including singlet oxygen yield, water vapor, iodine atoms, and translational temperature. In 1991, we began to investigate room temperature diode lasers as sensors for numerous gases, and have demonstrated monitors for over 30 gases since that time. Some of these were relevant to COIL, and we developed modules^{26,27} for three important species:

- Ground state oxygen
- Water vapor
- Iodine atoms.

The DFB lasers developed for telecommunications offer several advantages for rugged, fieldable COIL diagnostics. First, they produce narrow band (5 to 30 MHz), output that is rapidly (kHz rates) tunable over isolated rovibrational or rovibronic lines of the target species. Secondly, these lasers can be directly coupled to single mode fiber optic cables. This greatly simplifies the interface to COIL systems. Finally, as we discuss below, since the diode laser can scan an entire lineshape, the measurement becomes independent of both pressure and, to a large extent, temperature in the measurement volume.

The typical diode laser based sensor contains the diode laser, fiber optic delivery system, a room temperature solid state detector such as Si or InGaAs, and a PC controlled data acquisition and analysis system. A standard installation on a COIL device is shown in Fig. 10. Use of a fiber splitter allows us to produce several output fiber legs that can probe different regions of the COIL flow simultaneously.

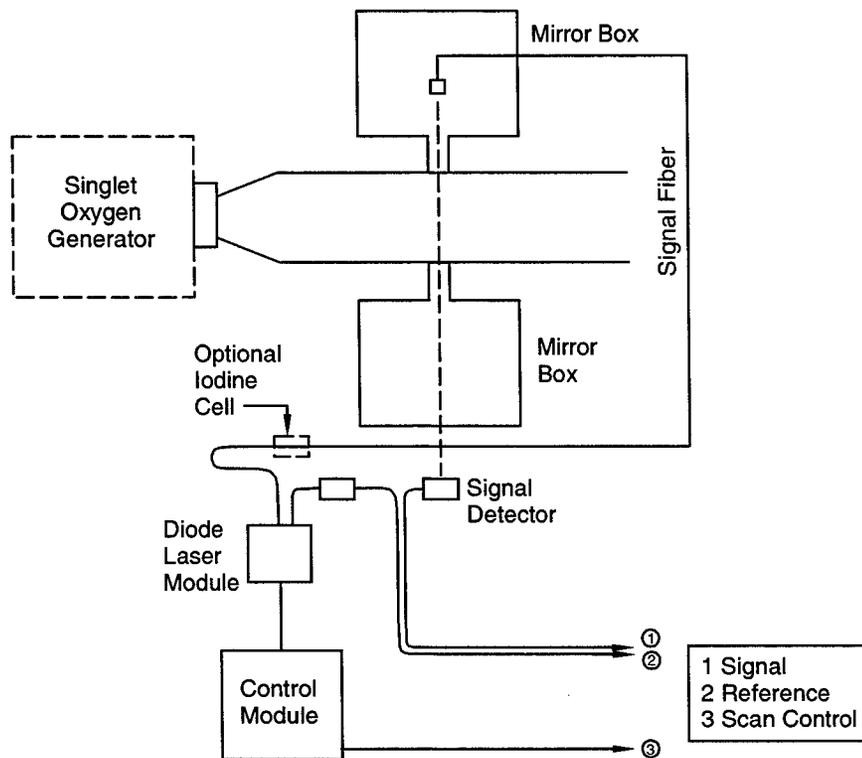


Fig. 10: Typical installation of a diode laser based COIL diagnostic. An Iodine Scan system is shown.

These systems use Beer's law to determine the concentration, N , of the target species as described in Eq. (5).

$$N = \frac{1}{S_T \ell} \int \ln \left(\frac{I_{0,v}}{I_v} \right) dv \quad (5)$$

where

S_T is the absorption linestrength

ℓ is the absorption pathlength

and $I_{0,v}$ and I_v are the initial and transmitted light intensities.

Note that since we scan the diode laser over the entire absorption feature, the integrated absorption is independent of the pressure because the integral under any absorption line is constant for constant number density of absorbers. The peak absorption is reduced as the pressure is increased, while the line broadens and the integral remains constant. Likewise, as the temperature increases, the Doppler width increases, but the integral under the absorption line remains constant. The absorption linestrength (S) has a temperature dependence due to the Boltzmann population distribution within the absorbing state. However, we have selected lines that have a minimal temperature dependence for typical COIL conditions.

The actual shape of the absorption curve is described by the lineshape function, $g(v)$. The lineshape function contains all the information with respect to the spectral shape of the absorption feature. In general, the lineshape can be described by a Voigt function which is a convolution of a Gaussian and a Lorentzian. Systematic fitting of the observed absorption lineshape will provide the Gaussian and Lorentzian full widths at half maximum (FWHM). The Gaussian FWHM can be used to determine the translational temperature in the measurement region. We have discussed this in prior

presentations and do not repeat it here.²⁸⁻³⁰ Several papers in this conference discuss temperature measurements using this approach.

In order to increase the accuracy of temperature measurements by this method, it is best to know the Lorentzian component of the linewidth. One can then deconvolve the Lorentzian to obtain the Gaussian component. To assist in this goal, we have made a series of detailed measurements of the collisional broadening coefficients²⁸⁻³⁰ of relevant absorption lines in oxygen, water vapor, and atomic iodine. Note that we define our measured broadening coefficients in terms of full width at half maximum (FWHM); i.e., (MHz/Torr). These are provided in Tables 2 through 4 below.

Table 2. Broadening coefficients for selected O₂(b←X) lines used in the Oxygen Scan diagnostic

Bath Gas	Oxygen Transition	Broadening Coefficient (MHz/Torr)	Line Shift Coefficient (MHz/Torr)
Oxygen	P5 P5	4.2	0.21
Oxygen	P19 P19	3.3	0.23
Helium	P5 P5	3.1	0.04
Neon	P5 P5	3.2	0.12
Argon	P5 P5	3.7	0.31
Nitrogen	P5 P5	4.1	0.29
Carbon dioxide	P5 P5	4.7	0.17
Chlorine	P5 P5	5.2	0.34
Water vapor	P9 Q8	5.0	---

Table 3. Broadening coefficients for the 1.3925 μm water vapor line used in the Water Scan diagnostic

Collision Partner	Broadening Coefficient (MHz/Torr)
H ₂ O	31.2
CO ₂	14.8
NH ₃	23.8
He	1.8
Ar	3.7
O ₂	4.8
N ₂	8.8
Air	7.6
Propane (C ₃ H ₈)	10.2
Ethane (C ₂ H ₆)	8.9
Ethane (C ₂ H ₄)	13.8
Proplene (C ₃ H ₆)	7.4
Methane (CH ₄)	7.6

Table 4. Broadening coefficients for several relevant gases on the (3,4) hyperfine line of atomic iodine

Bath Gas	Broadening Coefficient (MHz)
He	3.2
N ₂	5.5
O ₂	5.0

We have also measured the temperature dependence of the collisional linebroadening of the (3,4) hyperfine line in atomic iodine for both He and O₂ over the temperature range 300 to 775K. These values are:

$$(\Delta\nu/\Delta P_{\text{He}})_T = (3.2 \pm 0.3) \times (296/T)^{0.36}$$

and

$$(\Delta\nu/\Delta P_{\text{O}_2})_T = (5.5 \pm 0.6) \times (296/T)^{0.70}$$

These values can be used in the data reduction of absorption lineshapes including those in the cavity region where the temperatures are considerably lower than 300 K.

3.6 Raman spectroscopy

Gyls and Rabin³¹ have recently reported a complementary method for measuring the yield of singlet oxygen using Raman scattering. This method provides a direct measurement of the concentrations of both O₂(¹Δ) and O₂(³Σ) since the Raman cross sections for both these species are known. The typical set up is shown in Fig. 11. Since the Raman cross section is low, the method requires a high power laser and sensitive, wavelength dispersing optical detectors. Despite these potential drawbacks, Gyls and Rabin have demonstrated impressive results. There also a paper in this meeting that discussed Raman as an oxygen diagnostic for COIL.³²

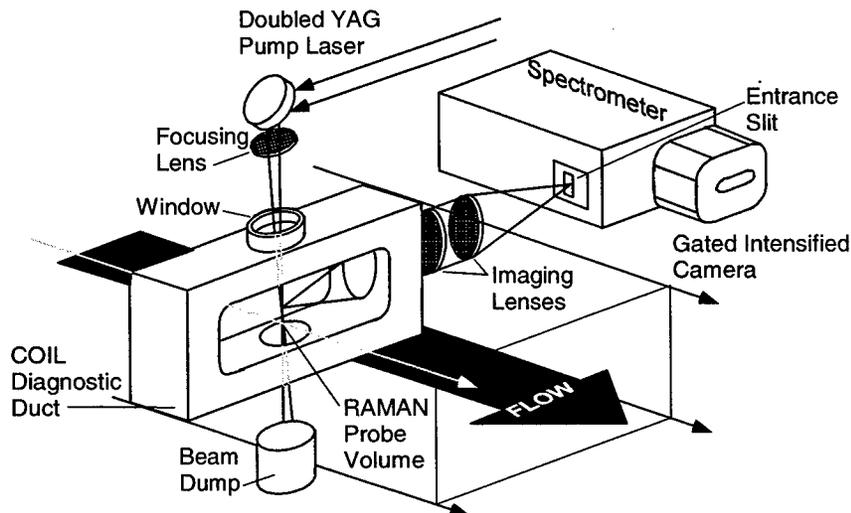


Fig. 11: Experimental setup for Raman imaging in COIL.

4. SUMMARY AND CONCLUSIONS

In this brief survey of the history of COIL diagnostics, I have attempted to provide a perspective of progress and recent developments. It is clear that we have all come a long way in developing tools to help investigate key aspects of COIL. We have seen a progression from the earliest chemiluminescence probes that led to the discovery of COIL to approaches that allow probing of ground state species, small signal gain, temperature, and spatially resolved parameters. These diagnostics, whatever flavor, will continue to aid the further development of advanced and more efficient COIL devices. Until the present time, most sensitive COIL diagnostics have been used to gain a better understanding of how this system operates, i.e. kinetic mechanisms and rates. Chemiluminescence-based diagnostics have been used for many years on active COIL devices as system "health" monitors. I suggest, that a fruitful path for future work in the diagnostics area would be to incorporate both passive and active diagnostics as part of a suite of open- and closed- loop feed back control systems to enhance the stability and reliability of COIL. Of course, this will require considerable engineering, but that is consistent with the high level of maturity that COIL has attained.

I would be remiss if I did not at least mention that advanced diagnostics might someday assist in the eventual resolution of the molecular iodine dissociation mystery. We may yet have some science to discuss at the 50th anniversary of COIL!

ACKNOWLEDGMENTS

I have had the privilege of working with many talented researchers in the field of COIL diagnostics and kinetics. I have already mentioned several in the body of the paper. In addition to them I would like to acknowledge Bob Shea and Dave Neumann, who were actively involved in some of the early diagnostics development work at AFWL. I would also like to mention Art Guenther and Pete Avizonis who recognized the value of advanced diagnostics and were very supportive. Don Ball, former director of AFOSR Chemical and Molecular Sciences, deserves a special thanks for generous and continual support during much of the period discussed. Gordon Hager of AFRL also has been very supportive of the diode laser diagnostics development. Finally, I would also like to thank my many colleagues at PSI including Bill Kessler, Phil Mulhall, Phil Keating, and Mark Allen for assisting in the development of the diode laser sensors.

REFERENCES

1. W.E. McDermott, N.R. Pchelkin, D.J. Benard, and R.R. Bousek, "An Electronic Transition Chemical Laser", *Appl. Phys. Lett.* **32**, 469, 1978.
2. D.J. Benard, W.E. McDermott, N.R. Pchelkin, and R.R. Bousek, "Efficient Operation of a 100-W Transverse Flow Oxygen Iodine Chemical Laser", *Appl. Phys. Lett.* **34**, 40, 1979.
3. R.J. Richardson and C.E. Wiswall, "Chemically Pumped Iodine Laser", *Appl. Phys. Lett.* **35**, 138, 1979.
4. W.E. McDermott, "Historical Perspective of COIL", SPIE Paper 4631-01, Gas and Chemical Lasers and Intense Beam Applications IV, San Jose, CA, January 2002.
5. M.C. Heaven, A.V. Komissarov, and V. Goncharov, "Mechanism and Kinetics of Iodine Dissociation in COIL", SPIE Paper 4631-02, Gas and Chemical Lasers and Intense Beam Applications IV, San Jose, CA, January 2002.
6. S.J. Arnold, N. Finlayson, and E.A. Ogryzlo, "Some Novel Energy-Pooling Processes Involving $O_2(^1\Delta_g)$ ", *J. Chem. Phys.* **44**, 2529, 1966.
7. R.G. Derwent and B.A. Thrush, "Excitation of Iodine by Singlet Molecular Oxygen", Part I, Mechanism of the I_2 Chemiluminescence", *J.C.S. Faraday II* **68**, 720, 1972.
8. R.G. Derwent and B.A. Thrush, "Excitation of Iodine by Singlet Molecular Oxygen", Part II, Kinetics of the Excitation of Iodine Atoms", *Discs. Faraday Soc.* **53**, 162, 1972.
9. R.G. Derwent and B.A. Thrush, "Measurements of $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g)$ in Discharge Flow Systems", *Trans. Faraday Soc.* **67**, 2036, 1971.
10. R.J. Donovan, F.G.M. Hathorn, and D. Husain, "Study of Electronically Excited Atoms, $I(5^2P_{1/2})$ in the Presence of Alkyl Iodides", *Trans. Faraday Soc.* **64**, 1, 1968.
11. J.J. Deakin and D. Husain, "Temperature Dependence of Collisionally induced Spin Orbit Relaxation of Electronically Excited Iodine Atoms, $I(5p^5^2P_{1/2})$ ", *J.C.S. Faraday II*, **68**, 1603, 1972.
12. A.T. Pritt, R.D. Coombe, D. Pilipovich, R. Wagner, D. Benard, and C. Dymek, "Chemical Generation of a Population Inversion Between the Spin Orbit States of Atomic Iodine", *Appl. Phys. Lett.* **31**, 746, 1977.
13. R.F. Heidner, C.E. Gardner, G.I. Segal, and T.M. El-Sayed, "Chain Reaction Mechanism for I_2 Dissociation in the $O_2(^1\Delta)$ I-atom Laser", *J. Phys. Chem.* **87**, 2348, 1983.
14. R.F. Heidner, C.E. Gardner, T.M. El-Sayed, and G.I. Segal, "Temperature Dependence of $O_2(^1\Delta) + O_2(^1\Delta)$ and $I(^2P_{1/2}) + O_2(^1\Delta)$ Energy Pooling," *J. Chem. Phys.* **74**, 5618, 1981.
15. P.M. Alsing, G. Simmons, and S.J. Davis, "Observations Concerning the Efficiency of the I_2 Dissociation by $O_2(^1\Delta)$ ", Laser Digest, AFWL TR- 82-88, 1982.
16. D.K. Neumann, P.K. Clark, R.F. Shea, and S.J. Davis, " O_2 Pressure Broadening of the Iodine $^2P_{1/2} \rightarrow ^2P_{3/2}$ Transition", *J. Chem. Phys.* **79**, 4680, 1983.
17. S.J. Davis and M.H. VanBenthem, "A Temperature Measurement Technique for COIL-IV", Laser Digest, AFWL TR-84-76, 1985.
18. S.J. Davis, "Dye Laser Pumped Atomic Iodine Laser", *Appl. Phys. Lett.* **32**, 656, 1978.
19. S.J. Davis and L. Hanko, "An I_2 Flow Rate Diagnostic for the Oxygen Iodine Laser", Laser Digest, AFWL-TR-79-104, 1979.

20. G.E. Hall, W.J. Marinelli, and P.L. Houston, "Electronic to Vibrational Transfer from $I^*(5^2P_{1/2})$ to $I_2(25 < V < 43)$ ", *J. Phys. Chem.* **87**, 2153, 1983.
21. S.J. Davis and M. VanBenthem, "Detection of Vibrationally Excited I_2 in the Iodine Dissociation Region of Chemical Oxygen-Iodine Chemical Lasers", *J. Phys. Chem.* **90**, 902, 1986.
22. H.V. Lilenfeld, "Oxygen Iodine Laser Kinetics", AFWL TR-83-01, Kirtland AFB, NM, 1983.
23. H.V. Lilenfeld, G.R. Bradburn, and F.E. Hovis, "Oxygen Iodine Laser Kinetics", AFWL-TR-84, 1984.
24. N.L. Rapagnani and S.J. Davis, "Laser Induced Fluorescence Measurements in a Chemical Laser Flowfield", *AIAA Journ.* **17**, 1402, 1979.
25. H.V. Lilenfeld and R.J. Richardson, "The ESR Spectrum and Linewidth Measurements of Atomic Iodine", *J. Chem. Phys.* **70**, 3859, 1979.
26. M.G. Allen, K.L. Carleton, S.J. Davis, W J. Kessler, and K.R. McManus, AIAA 25th Plasmadynamics and Lasers Conference, Colorado Springs, CO, June 1994.
27. S.J. Davis, M.G. Allen, W.J. Kessler, K.R. McManus, M.F. Miller and P.A. Mulhall, "Diode Laser-based Sensors for Chemical Oxygen Iodine Chemical Lasers", SPIE paper 2702-17, OE-Lase Conference, San Jose, CA, 1996.
28. S.J. Davis, W.J. Kessler, , and M. Bachmann, "Collisional Broadening of Absorption Lines in Water Vapor and Atomic Iodine Relevant to COIL Diagnostics," SPIE Paper No. 3612-25, The International Society for Optical Engineering, San Jose CA, 1999.
29. S.J. Davis, W.J. Kessler, M. Bachmann, P.A. Mulhall, "Collisional Broadening Coefficients for Oxygen and Water Absorption Lines Used in COIL Diagnostics," SPIE Paper 3268-80, Gas and Chemical Lasers and Intense Beam Applications, San Jose, CA, 1998.
30. S.J. Davis, W.J. Kessler, and P.K. Keating, "Progress in the Development of Sensors for COIL Devices", Paper 3931-24, SPIE Gas Phase and Chemical Lasers and Intense Beam Interactions, San Jose, CA, 2000.
31. V.T. Gyls and L.F. Rubin, "Direct Measurement of $O_2(a^1\Delta)$ and $O_2(X^3\Sigma)$ in Chemical Oxygen Iodine Lasers with use of Spontaneous Raman Imaging", *Appl. Opt.* **37**, 1026, 1998.
32. W. Zhao, F. Sang, and L. Duo, "Measurement of Chemical Oxygen Iodine Laser Singlet Oxygen Generator Parameter using Raman Spectroscopy", Paper 4631-25, Gas and Chemical Lasers and Intense Beam Applications IV, San Jose, CA, January 2002.