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FRANK J. SEILER RESEARCH LABORATORY

FJSRL TECHNICAL REPORT-76-0011
AUGUST 1976

NEW GAS LASERS

PROJECT 2303

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AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

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Delta

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report concludes studies begun under FJSRL Work Unit 7903-03-69. Additional work in this area will be continued as FJSRL Task 2303-F4. The objective of this study is to develop a chemical method for producing $O_2('\Delta g)$ in the gas phase and evaluating the $O_2('\Delta g)$-I transfer chemical laser. A heterogeneous flow reactor was designed in which 90% H_2O_2 was coated on a glass substrate and exposed to a gas flow of Cl_2 or Cl_2O. The oxygen generated in the gas phase from the alkaline hypochlorite-peroxide reaction was detected down stream of the reactor via Electron Paramagnetic Resonance Spectroscopy. A yield of 11% $O_2('\Delta)$ to total

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20. ABSTRACT (continued)

oxygen was observed for the Cl_2/H_2O_2 system. This represents an intrinsic reaction efficiency of 16%. The lower total yield arises from the contribution of O_2 produced by the decomposition of the peroxide solution. The highest total yield for the Cl_2O/H_2O_2 system was 8.4%. The latter system produced O_2('Δg) without the addition of base to the H_2O_2 (5% yield).

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FJSRL-TR-76-0011

NEW GAS LASERS

FINAL REPORT

William E. McDermott
Richard E. Lotz
Myron L. DeLong
David M. Thomas

Technical Report FJSRL-TR-76-0011

August 1976

FOREWORD

This report was prepared by the Department of Chemistry and Biological Sciences, United States Air Force Academy, Colorado. This work was initiated under Frank J. Seiler Research Laboratory, Directorate of Chemical Sciences Research Project No. 7903, "Chemical Synthesis and Characterization," Task 7903-03, "USAF Academy Physical Sciences Research," Work Unit No. 7903-03-69, "Chemiluminescent Gas Phase Reactions," with Capt William E. McDermott, Capt Richard E. Lotz, Capt Myron L. DeLong, and Capt David M. Thomas (Department of Physics, United States Air Force Academy) acting as investigators. Funding support from the Air Force Weapons Laboratory (ALD) under Project Order No. 75-273 as well as Research Project 7903 is acknowledged.

This report covers work accomplished from 30 September 1975 to 30 July 1976 and is the final report for this work unit. Additional investigations in this area will be continued under Frank J. Seiler Research Laboratory, Directorate of Chemical Sciences, Task 2303-F4, "Molecular Dynamics." This manuscript was released by the authors in August 1976 for publication as a technical report.

This technical report has been reviewed and is approved.

Ronald E. Channell	
RONALD E. CHANNELL, Capt, USAF Director of Chemistry Research Department of Chemistry and Biological Sciences US Air Force Academy	BEN A. LOVING, LtCol, USAF Director, Chemical Sciences Frank J. Seiler Research Laboratory (AFSC)

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I. INTRODUCTION

Previous investigations have shown that excited molecular oxygen ($O_2['\Delta g]$) can be produced chemically in solution via the absorption of $Cl_2(g)$ by a solution of basic H_2O_2. The production of $O_2('\Delta g)$ is important since it has been predicted theoretically[2] that energy transfer from this species can pump an iodine atom laser ($^2P_{1/2}-^2P_{3/2}$). The threshold for this process has been predicted[3] to be 25% excited oxygen to total oxygen for realistic lasing conditions. This energy transfer must be carried out in the gas phase; however, only liquid phase reactions have been known to produce excited oxygen in sufficient yield.[4,5,6]

As the lifetime of $O_2('\Delta g)$ has been measured[7,8] to be 2μ sec in aqueous solution, an excited oxygen molecule can only diffuse approximately 1×10^3 Å before being quenched. To allow a reasonable fraction of $O_2('\Delta g)$ to escape into the gas phase thus requires the liquid reactants to be mixed in such a way as to have a mean distance of 10^3 Å from the source of the singlet oxygen production to the surface of the reagents. It is difficult to mix liquid reagents, in vacuo, on such a fine scale.

We have developed an alternative approach. The reactants required to produce singlet oxygen are formed, in situo, in a narrow layer on the surface of the liquid phase by utilizing the slow diffusion of gases in a liquid. The gases used are Cl_2 and Cl_2O, both of which hydrolyze in aqueous solution to form the hypochlorite ion. The liquid phase chosen was a concentrated H_2O_2 solution (90% or less) to which was added a small amount of NaOH. The reaction between hypochlorite ion and alkaline H_2O_2 is reputed[9] to produce yields of $O_2('\Delta g)$ in excess of 60%. The reaction mechanism has been investigated[7] in weak solutions of H_2O_2 (3%), but the reaction in concentrated H_2O_2 has not been studied. It is known via isotope studies[10] that the excited oxygen is derived cleanly from the H_2O_2.

II. EXPERIMENTAL PROCEDURE

A. Chemical Generation

A flow reactor, shown in Figure 1, was designed to provide a quasi-continuous production of $O_2('\Delta g)$. The reactor was loaded with 15-25 ml of H_2O_2, usually made basic by the addition of NaOH and about 100 ml of loosely packed glass helices. The ground glass joints were covered with a thick layer of Kel-F[11] grease allowing the reactor to turn freely when driven by a stirrer motor. Turning the reaction vessel allows a recoating of the glass helices. The atmospheric pressure on the reactor ends slowly forces the grease out of the joints so that after a period of about one-half hour, the reactor will not be turned by the drive motor. A steady production of $O_2('\Delta g)$ is observed prior to this time.

After loading and mounting the reactor, the system is pumped down after opening a bypass valve connecting points A and B (Figure 1). This minimizes migration of the H_2O_2 down the outlet tube. The valve is closed in normal operation. A cold trap with dry ice and acetone is placed down stream of the reactor to trap H_2O_2 and H_2O. After the down stream pressure stabilizes, Cl_2[12] gas (unpurified) or Cl_2O (see section II.C) is allowed to flow through the reaction tube. In the latter case, the Cl_2O is maintained in a dry ice/acetone bath (vapor pressure ∿1 Torr) and carried through the reactor by a flow of He. Adsorption of either species on the liquid phase generates $O_2('\Delta g)$ which is observed down stream of the reaction vessel using a Varian 4502 Electron Paramagnetic Resonance Spectrometer.

B. EPR Measurements

The details of concentration measurements via EPR spectroscopy are covered in a companion report.[13] The use of magnetic field modulation and phase sensitive detection produces a spectrum which is approximately the derivative of a Lorentzian absorption curve at low modulations. It is actually the first harmonic of the Fourier expansion of the absorption curve at the modulation frequency.[14] A typical spectrum is shown in Figure 2. The peak to peak width and signal height can be related directly to the number density of the absorbing species.[15] When comparing different species which undergo magnetic dipole transitions, all instrumental factors can be determined by measuring the area of the absorption curve arising from known pressures of a stable species ($O_2[^3\Sigma g]$)[16].

A Varian 4502 Electron Paramagnetic Resonance Spectrometer was used in these investigations. Two different sample cavities were used, a large sample access cavity (2.54 cm dia) and a standard Varian V-4531 cavity (1.10 cm dia). The smaller cavity is less sensitive but allows the use of 7 inch tapered pole pieces enabling use of a higher resonant magnetic field. The higher field (∿23 kg) permits the measurement of $I(^2P_{1/2})$.

Figure 3 shows a typical experimental set-up (large cavity). The smaller cavity configuration is identical except for an adapter section which reduces the flow diameter to 1.0 cm in the region of the magnetic field.

Figures 4 and 5 show plots of the peak area versus pressure for the $O_2(^3\Sigma)$ reference line in each cavity. The pressures were measured with a McLeod gauge and the area at zero pressure corresponds to the background pressure of the system (∿50 microns of air). Experiments were run utilizing a microwave discharge (2.45 GHZ) to produce $O_2('\Delta g)$.[17]

The amount of $O_2(^1\Delta g)$ obtained using theoretical expressions[13,18] for the line strength agreed within experimental error with the amount calculated from the observed decrease in the ground state oxygen signal when the discharge was turned on.

C. Synthesis of Cl_2O

Chlorine (I) oxide is a reddish bromine-like liquid which boils at 2°C.[19] It is formed by the reaction[20]:

$$2HgO + 2Cl_2 \rightarrow HgO \cdot HgCl_2 + Cl_2O \qquad (1)$$

The apparatus shown in Figure 6 was used for the synthesis. The HgO (yellow form)-glass mixture was dried in an oven and packed loosely into the U-tube. A regulator pressure of 4 psig and a reading of 80 (glass ball) on the flowmeter was used for the Cl_2 flow. The air flow rate was adjusted to be approximately twice the Cl_2 flow rate. This apparatus produces about 10 ml of Cl_2O per hour.

III. RESULTS

A. Cl_2

Figure 7 illustrates the percentage of $O_2('\Delta g)$ obtained versus Cl_2 flow rate as determined via the EPR measurements. The crosses represent data obtained when the reactor was filled with loosely packed glass helices and the X marks data obtained when loosely packed with glass wool. In both cases, about 10 ml of 90% H_2O_2 made basic (see Appendix) with 1-2 ml of 6 N NaOH was used. There was no apparent increase in Cl_2 utilization seen when the glass wool was used. This is likely due to channeling in the glass wool. The actual partial pressures of O_2 observed in each case are tabulated in Tables 1 and 2. The

Table 1. O_2 Production as a Function of Cl_2 Flow for Glass Helices

Flow Rate (cm^3/sec)	$O_2(^3\Sigma)$ (Microns)	$O_2('\Delta)$ (Microns)	Percent above background decomposition (100μ)
0	134	-	-
1.1	115	2.0	(11.8)
5.9	378	27.5	9.0
12.0	177	14.9	16.2
13.2	255	28.7	15.6

Table 2. O_2 Production as a Function of Cl_2 Flow for Glass Wool Substrate

Flow Rate (cm^3/sec)	$O_2(^3\Sigma)$ (Microns)	$O_2('\Delta)$ (Microns)	Percent above background decomposition (180μ)
0	188	-	-
1.5	183	1.2	(28.6)
2.5	396	12.6	5.5
Repacked glass wool			
0	182	-	-
1.5	277	2.3	2.3
1.7	287	7.1	6.2
2.5	367	18.0	8.8

fraction of generated oxygen (above the background decomposition of the H_2O_2) is also tabulated. In both bases, the fraction of the Cl_2 flow which reacted was small. At a flow rate of 13.2 $cm^3 sec^{-1}$, a down stream total pressure, largely due to Cl_2, of 2 Torr was observed. No $O_2('\Delta g)$ generation was observed unless base was added to the 90% H_2O_2. In all of these experiments the observed $O_2('\Delta g)$ fraction represents a minimum intrinsic reaction yield as there is likely some deactivation between the reactor and the 1 inch flow tube through the EPR. A large portion of this is likely occurring in the 6 feet of 1/4 inch diameter tygon tubing used to connect the down stream side of the cold trap to the EPR flow tube.

B. Cl_2O

While the generation of $O_2('\Delta g)$ via the action of $Cl_2(g)$ on alkaline H_2O_2 has been observed previously, we report here the first observation of $O_2('\Delta g)$ arising from the action of $Cl_2O(g)$ on alkaline H_2O_2. Table 3 summarizes the Cl_2O data obtained. This data was obtained in the smaller EPR cavity necessitating the use of high modulation. We have not completely calibrated the EPR under these conditions, therefore, can only present relative data. While the $O_2('\Delta g)$ fractions are smaller than the fractions obtained with $Cl_2(g)$,

Table 3. $O_2('\Delta)$ Fraction Observed in the Reaction of Cl_2O on 90% H_2O_2

Basic H_2O_2	$[O_2('\Delta)]/[O_2(^3\Sigma)]$
(1)	0.069
(2)	0.084
90% H_2O_2, no base	
(3)	0.042

the down stream pressures are considerably less, being on the order of 0.3 Torr in the best case. Furthermore, some yield of $O_2('\Delta)$ was obtained with no added base. In these runs no carrier gas flow was used. A low flow of He was observed to increase the yield slightly.

C. I_2 Titration

Several qualitative experiments involving the titration of I_2 into discharged oxygen were run. Seven of the 18 $I(^2P_{3/2})$ EPR transitions were identified. No attempt was made to locate the other transitions. The $I(^2P_{1/2})$ transitions at high field were not observed. This result is to be expected since a rough estimate of the line intensity indicates that the signal level would be below the noise level. We did note, however, that maximization of the $I(^2P_{3/2})$ signal resulted in a complete depletion of the $O_2('\Delta)$ signal. Since the only mechanism for I atom production is

$$O_2('\Sigma) + I_2 \rightarrow 2I + O_2(^3\Sigma) \tag{2}$$

and the only deactivation reaction of $O_2('\Delta)$ that produces $O_2('\Sigma)$ is

$$O_2('\Delta) + I(^2P_{1/2}) \rightarrow O_2('\Sigma) + I(^2P_{3/2}) \tag{3}$$

we have at least an indirect indication of the production of the excited iodine atom.

IV. DISCUSSION

These experiments indicate that the intrinsic yield of the OCl^-/H_2O_2 reaction is greater than 16%. Since the hydrolysis of $Cl_2(g)$ and $Cl_2O(g)$ yield the same product, it is expected that $Cl_2O(g)$ yields will approximate those observed in the $Cl_2(g)$ experiments. The failure of $Cl_2(g)$ to produce $O_2('\Delta)$ in pure (non basic) H_2O_2 supports the mechanism[21]

$$Cl_2 + OH^- \rightarrow HOCl + Cl^- \tag{4}$$

for the hydrolysis of Cl_2. In contrast, the hydrolysis of Cl_2O to produce HOCl does not require the hydroxide ion:

$$Cl_2O + H_2O \rightarrow 2HOCl \tag{5}$$

Further, reaction (4) indicates that Cl_2O is theoretically twice as efficient as Cl_2 in producing HOCl.

The reactions were carried out in 90% H_2O_2 made basic with NaOH. In most cases the pH of the resulting solution was between 5 and 6. Kajiwara and Kearns[7] have determined that the optimum pH for the production of $O_2('\Delta)$ lies at about pH = 10. A more dilute peroxide solution adjusted nearer to this pH could therefore produce a higher $O_2('\Delta g)$ yield than observed in these experiments.

APPENDIX

pH CONTROL IN 90 PERCENT H_2O_2

Ninety percent hydrogen peroxide is an acidic solvent as shown by its pH of about 0.5.[22] We have measured a value of 1.4 for the (nominally) 90% H_2O_2 used in these experiments. Due to the well known leveling effect of a solvent, it is difficult to raise the pH of 90% H_2O_2 without the addition of large quantities of base. Using a standard Beckmann pH meter, the addition of 5 ml of 6 N NaOH to 50 ml of H_2O_2 raised the pH to about 5.6. The addition of 20 ml raised it only to 6.7. This greatly accelerated the decomposition causing the peroxide-base mixture to boil within 5 minutes. The validity of glass electrode in pH measurements of concentrated peroxide solutions has been established.[23]

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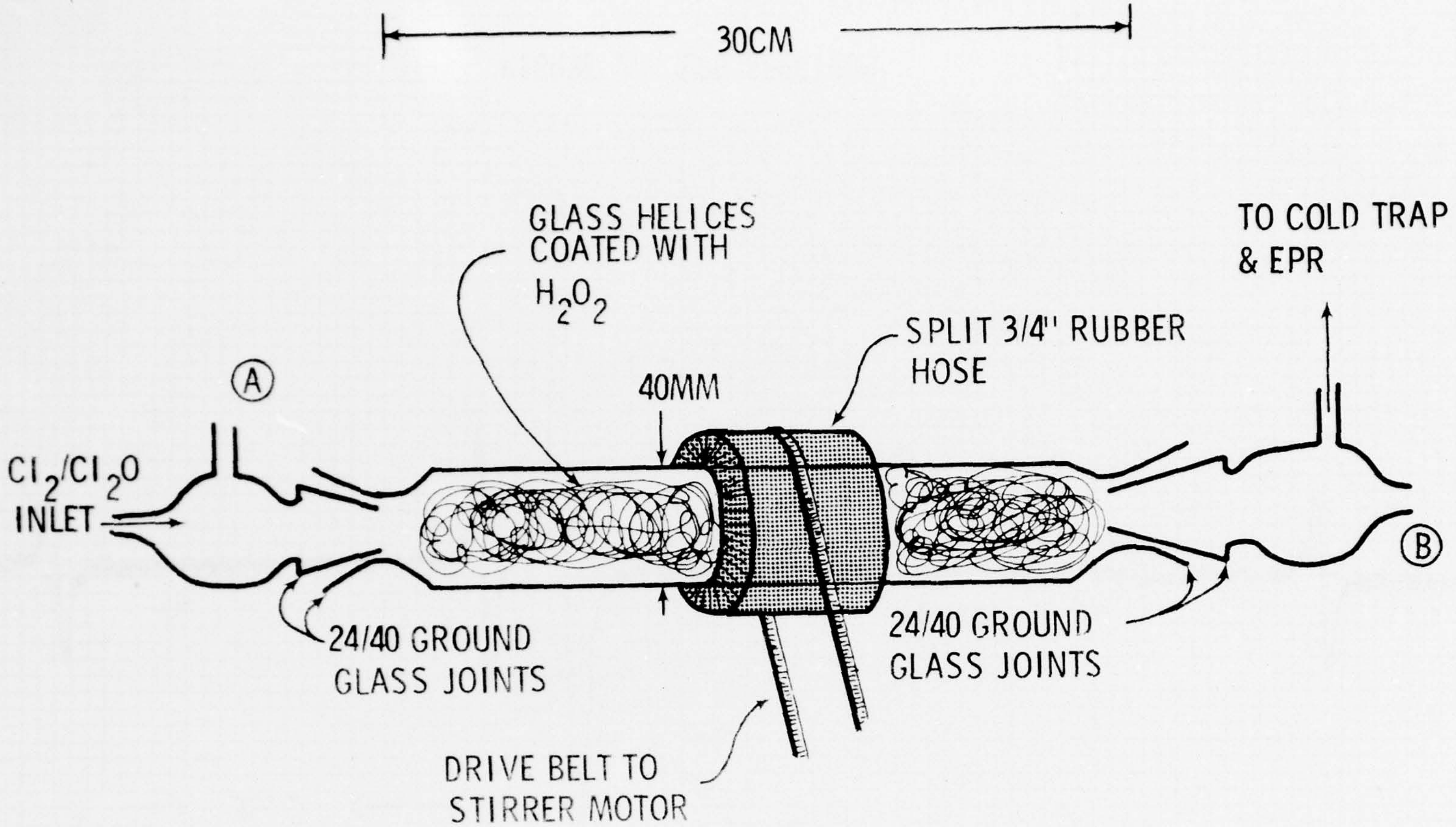

FIGURE 1 - FLOW REACTOR

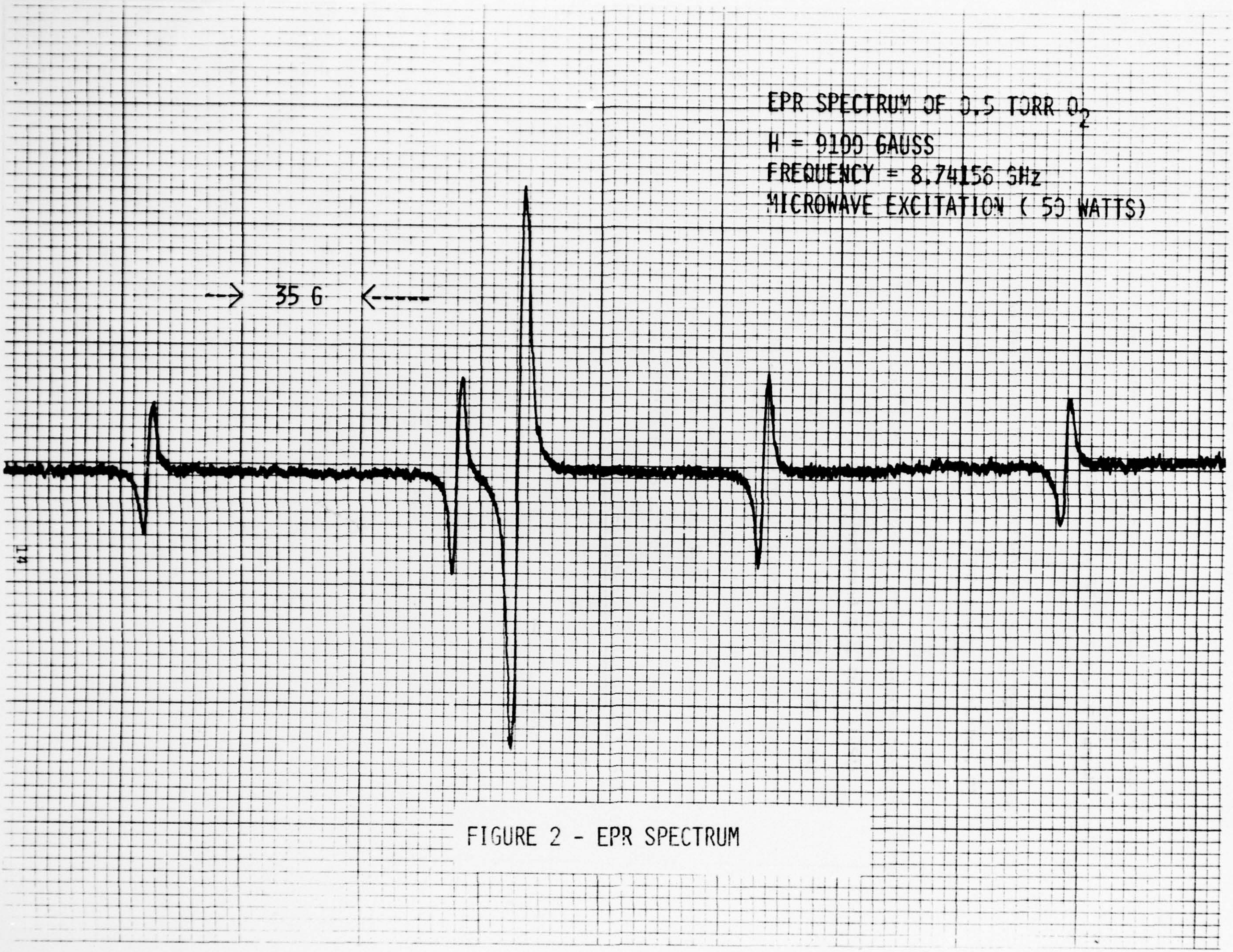

FIGURE 2 - EPR SPECTRUM

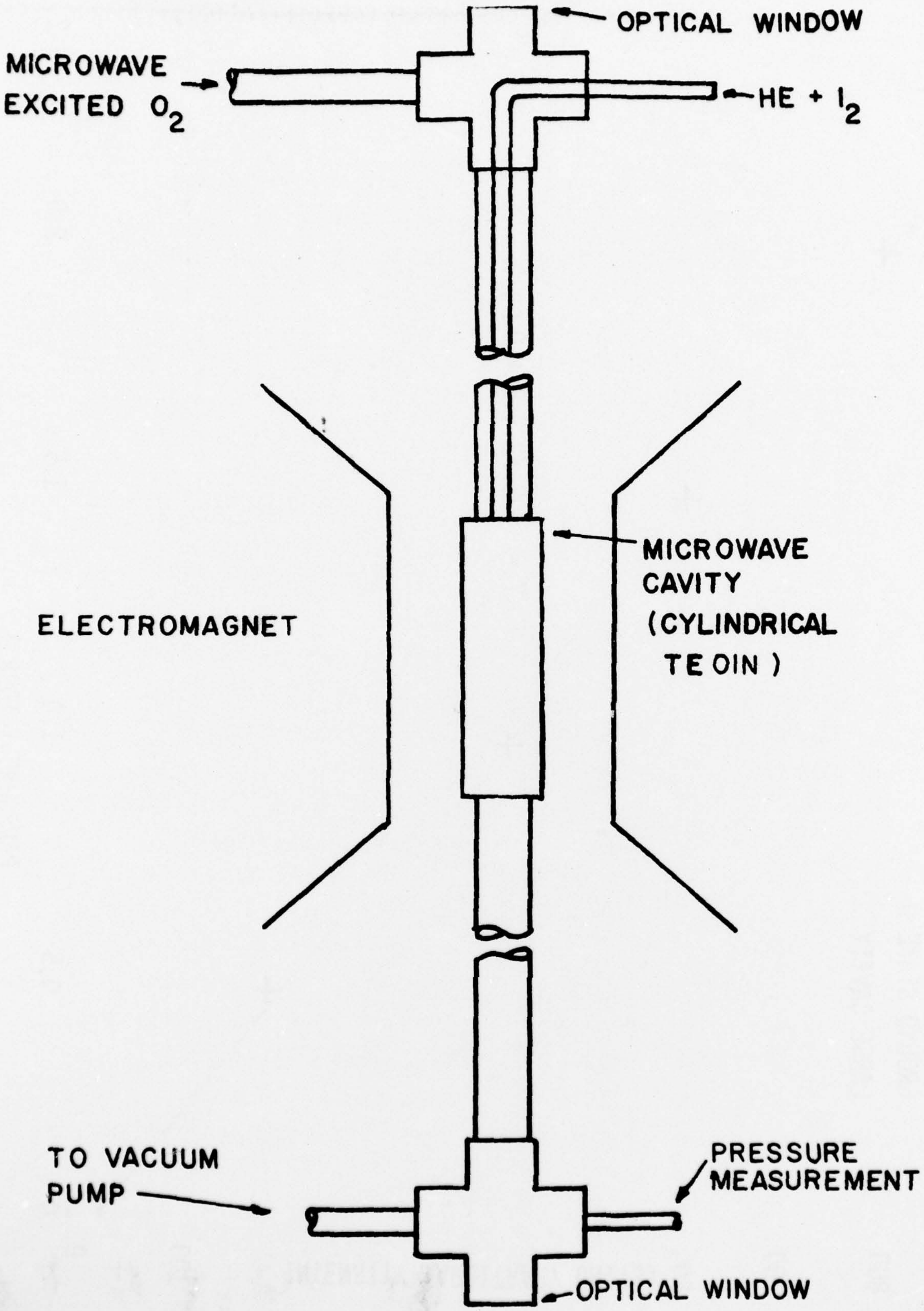

FIGURE 3 - EXPERIMENTAL SET--UP

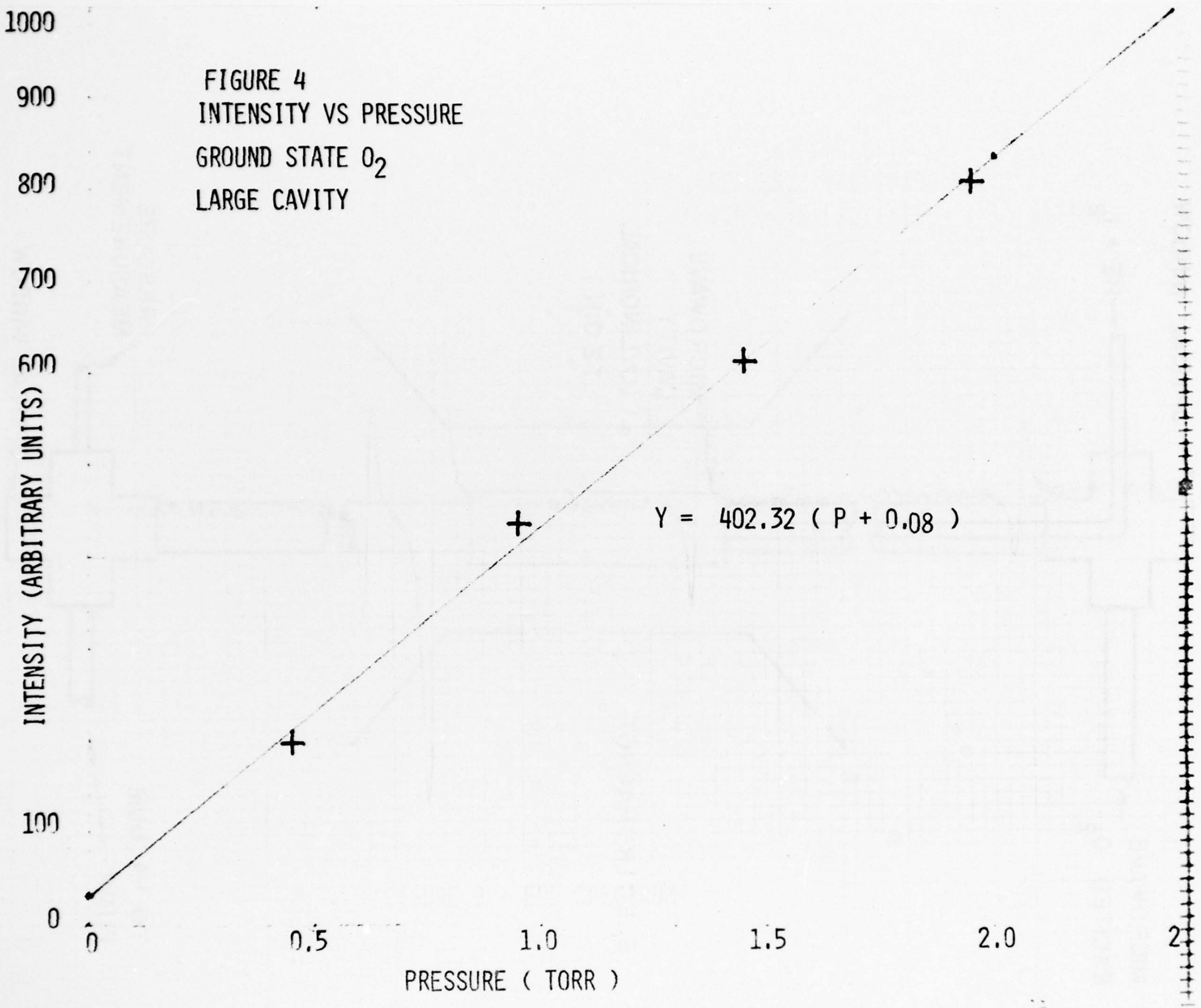

FIGURE 4
INTENSITY VS PRESSURE
GROUND STATE O_2
LARGE CAVITY

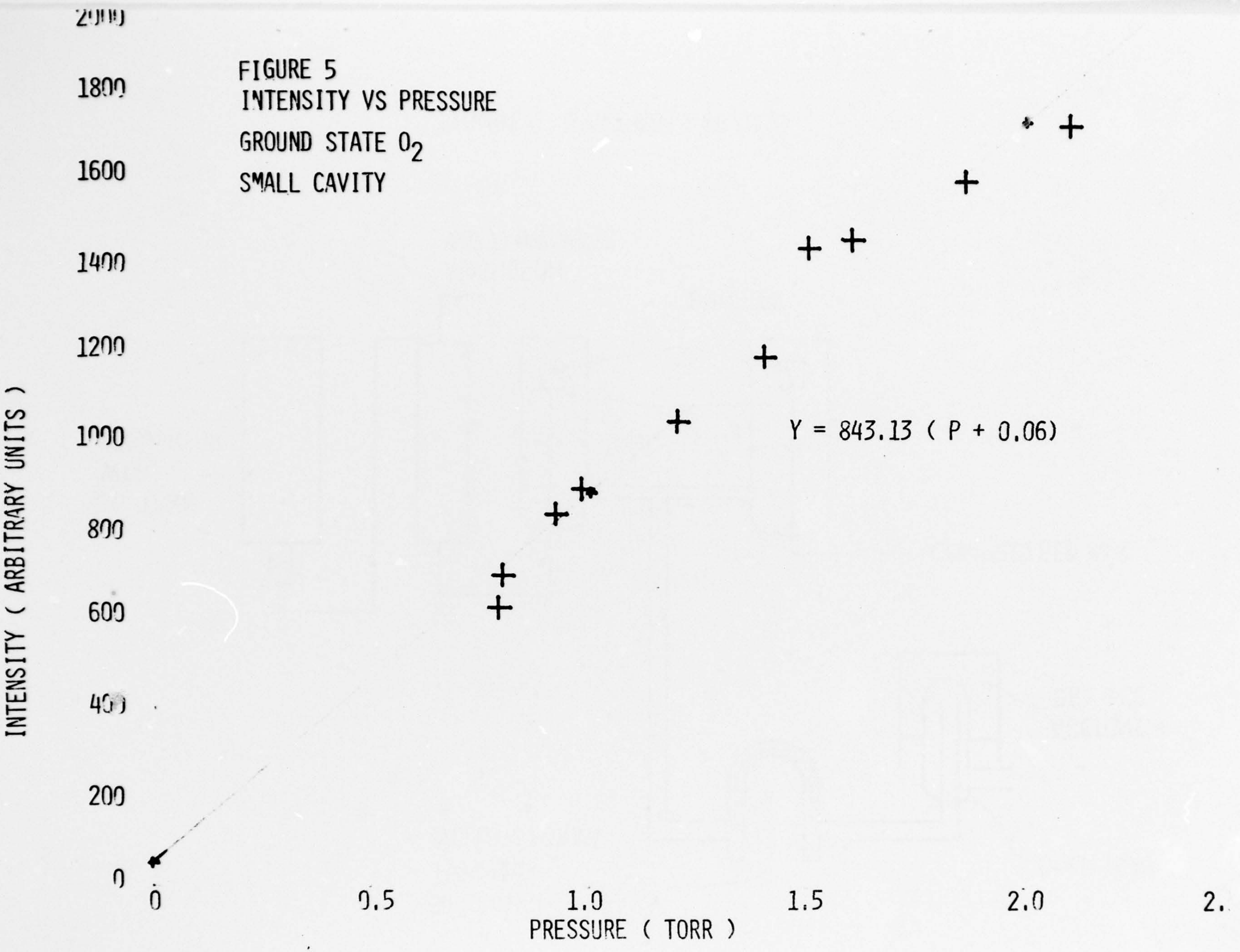

FIGURE 5
INTENSITY VS PRESSURE
GROUND STATE O_2
SMALL CAVITY

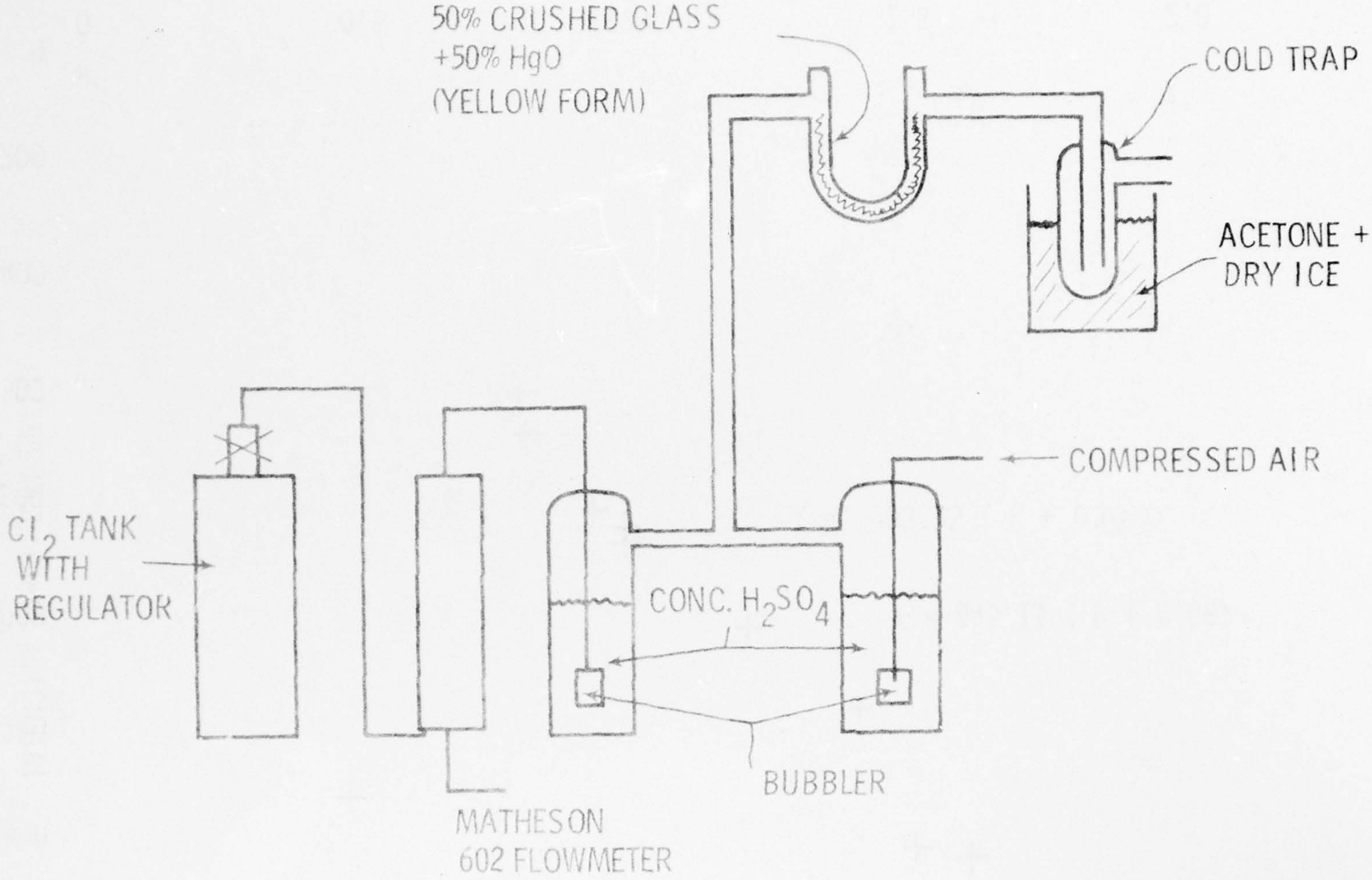

FIGURE 6 - SYNTHESIS OF Cl_2O

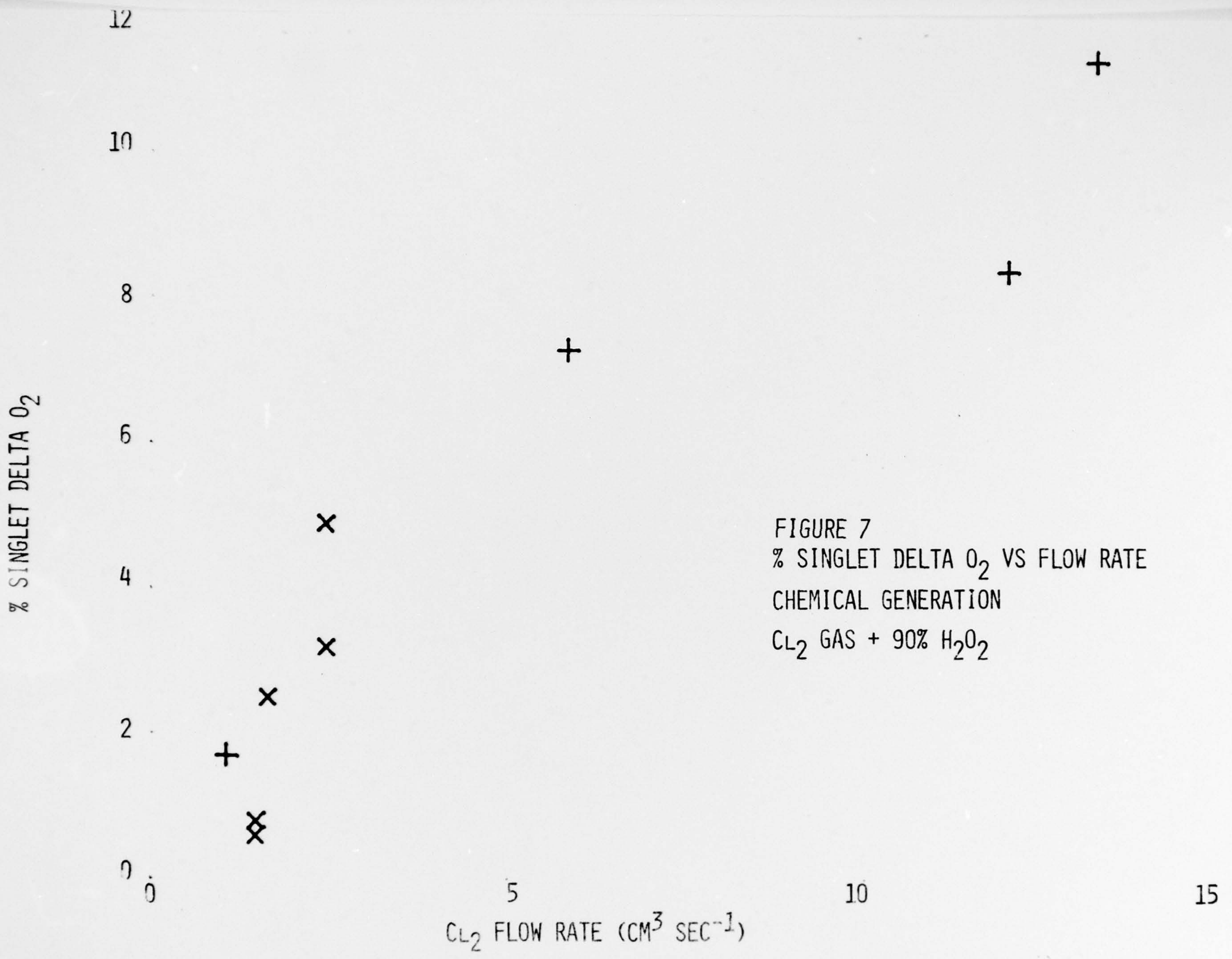

FIGURE 7
% SINGLET DELTA O_2 VS FLOW RATE
CHEMICAL GENERATION
CL_2 GAS + 90% H_2O_2