INVESTIGATION OF LASER-INDUCED FLUORESCENCE DETECTION OF BORON OXIDES IN FLAMES

THESIS

Jong W. Cha
Major, ROKAF

AFIT/GEO/ENP/89J-1

DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY
AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

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THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
Air University
in Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Electrical Engineering

Jong W. Cha
Major, ROKAF

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Preface

The purpose of this research was to demonstrate that the laser-induced fluorescence (LIF) technique could be used for determining the concentration of boron compounds in an atmospheric-pressure, boron seeded flame. The motivation for this research was to provide a useful tool with which to prove the detailed combustion chemistry of boron fuels.

The two most important reaction intermediates in the boron oxidation process, BO and BO_2, were searched. First, the optimization of LIF diagnostics of BO_2 as demonstrated by Greg R. Schneider was attempted. Then, the feasibility of LIF detection of BO was investigated.

In performing the experiment and writing this thesis, I have had a great deal of help from others. I am deeply indebted to my faculty advisor, Dr. Won B. Roh for his guidance and continuing patience in times of need. I also wish to thank my thesis committee, Dr. William F. Bailey and Mr. Sigmund Kizirnis. A word of thanks is also owed to Rick Patton of the Physics Department. A mention of thanks and indebtedness is due to Dalayr W. Height and David Martin for their assitance in thesis editing. Finally, I wish to thank my wife Yun, and my children, Jeong H. and Seong H. for their understanding and concern on those many nights when I was tied to my desk with work.

Jong W. Cha

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Abstract

The puopose of this project was to demonstrate the feasibility of a laser-induced fluorescence (LIF) technique for determining the concentration of boron compounds in an atmospheric-pressure, boron seeded flame. Such a demonstration would provide a useful tool to investigate the detailed combustion chemistry of boron fuels. The two radical species which are thought to be the most important reaction intermediates in the boron combustion process, BO and BO_2, were sought.

A burner was used to produce a CH_4/dry air/O_2 flame, then BCl_3 was added to the flame. This burner was movable in two directions, so various regions of the flame could be investigated easily.

A tunable pulsed dye laser which was pumped by an excimer laser was used to match the absorption bands of BO and BO_2. Good LIF signals of BO_2 were readily achieved, then the optimum band for LIF diagnostics of BO_2 was sought. The excitation of the $(10^0 0\text{-}00^0 0)$ band followed by fluorescence detection of the $(10^0 0\text{-}20^0 0)$ band was the optimum choice. Although a rather extensive search for LIF signal of BO was conducted, no LIF signal attributable to BO was detected. The most possible reason for this negative result was thought to be a heavy quenching under a high-pressure environment.

INVESTIGATION OF LASER-INDUCED FLUORESCENCE DETECTION OF BORON OXIDES IN FLAMES

I. Introduction

In recent years, solid fuels for air breathing propulsion systems have received considerable attention because of their potential for greater energy release per unit volume or weight in comparison with purely liquid fuels. A number of solids such as aluminum, boron, carbon, magnesium, etc., are possible candidates for fuel mixtures. Boron, however, is the most attractive candidate because of its superior volumetric and/or gravimetric heating value. According to King (1), boron possesses the greatest energy density in terms of calories per gram and/or calories per cubic centimeter.

TABLE I

Comparison of Heating Values (1:294)

Fuel	Gravimetric Heating Value, cal/g	Volumetric Heating Value, cal/cc
JP-5	10,150	8,230
Carbon	7,830	17,700
Shelldyne-H	9,860	10,000
$(CH_2)_n$	10,400	9,600
Magnesium	5,910	10,300
Aluminum	7,420	20,000
Boron	13,800	32,200

This research intends to provide a useful tool to investigate the detailed combustion chemistry of boron fuels.

II. Background

Boron was discovered in 1808 by the French chemists Louis Gay-Lussac and Louis Jacques Thenard (2:288). It is the first and lightest member of the group of elements located in column IIIA of the periodic table. Its atomic number is 5, and its atomic weight is 10.811. It is found in concentrated form in the salts of the ocean and in dry beds of ancient inland seas.

The earliest observation on boron combustion is that of Talley (3) in the late 1950's. He measured rates of oxygen consumption for boron rods that were 1 mm in diameter and electrically heated to temperatures between 1500° K and 2300° K, at atmospheric pressure.

In the late 1950's, Kaskan and Millikan used spectroscopy to analyze flames of trimethyl-borate (4). They proposed BO_2 as an important reaction intermediate.

Later, in the 1960's and early 1970's, Macek and Semple used time-exposed photographs to study boron combustion (5). They ignited boron particles, approximately 40 microns in diameter, at atmospheric pressure in hot (2200° K to 2900° K) oxidizing gases of various compositions, in a specially designed gas burner. They verified a existence of the two-stage combustion mechanism and obtained burning times for each stage. The first stage of combustion, which was a slow ignition phase involving the removal of the oxide coating of B_2O_3. The second stage, which was a rapid burning phase, was the burning of the clean boron particle.

Mohan and Williams also used a photographic method to study a burning rate of boron particle (6). From high-speed photographs of the ignition and combustion of laser-ignited boron particles in the 100 micron-diameter range, they found the amorphous particles burned much more rapidly, having an almost explosive combustion, while the crystalline boron, which was used by Macek and Semple (5), went through the relatively long two-stage process. The amorphous structure being highly nonuniform has a much greater surface area than the crystal, so it absorbs more laser radiation and oxidizes much more rapidly.

Emission spectroscopy was the preferred diagnostics for many boron combustion researchers. McLain and Evans reported that the presence of hydrogen in the combustion products would reduce the specific impulse and the heat of reaction of the fuel (7). They used a simulated rocket flame that was burning Hybaline B-3 (CNB_2Be) in a hydrogen-oxygen gas mix to identify major combustion species such as BO_2, OH, CO_2, H_2O, and HBO_2. Morrison and Schellar found a BO peak around 340 nm in the hottest part of the boron/JP-4 flame (8). They reported the peak around 460 nm, but didn't assign it to BO. Eisenreich and Liehmann observed the reaction of boron with time resolved emission spectroscopy in the range of 200 nm to 550 nm for different burning processes (9). They could identify emitted bands of BO, BO_2, HBO_2, CO, and CO_2.

Schadow (10) and Ormand (11) studied boron cloud combustion. Schadow used boron powder entrained in $H_2/O_2/N_2$ or $CO/O_2/N_2$ gas flows in a large area combustion tunnel. Ormand established a one-dimensional analytical model for the steady state combustion of multiparticle cloud of boron in air. These studies provided limited spectroscopic or reaction rate data.

King and Macek described the ignition and combustion characteristics of pure boron by analyzing the condensed exhaust products from rocket motor firings using boron-containing propellants (12). They found the condensed products behaved much like the original boron except for much faster ignition times.

Miller investigated the chemistry of boron combustion products with particular emphasis on the phenomena preceding and accompanying nucleation in expanding flows (13). He showed that HBO_2 and its higher order compounds were the primary combustion product. The dehydration corresponding to the overall process $2HBO_2 \dashrightarrow B_2O_3 + H_2O$ required many steps.

King (1) and Glassman (14) mentioned boron combustion processes. The boron oxidation starts with the formation of BO. The BO is then further oxidized via two channels:

$$BO + O_2 \text{ ---> } BO_2 + O + 4.1 \text{ kcal/mole}$$

$$BO + BO_2 \text{ ---> } B_2O_3 + 130.0 \text{ kcal/mole}$$

In the presence of H_2O, additional faster reactions would dominate:

$$M + BO + OH \longrightarrow HBO_2 + M + 142.8 \text{ kcal/mole}$$

$$HBO_2 + BO \longrightarrow HBO + BO_2 - 50.3 \text{ kcal/mole}$$

$$BO_2 + BO \longrightarrow B_2O_3 + 130.0 \text{ kcal/mole}$$

$$M + HBO \longrightarrow BO + H + M - 73.0 \text{ kcal/mole}$$

Both of these reaction chains shows BO and BO_2 to be fundamental intermediates.

To date, most of the experiments have not taken place in an actual flame condition. Most approaches for analyzing the boron combustion have been limited to survey emission spectroscopy and photographic records of boron particle burn times.

Recently, Schneider (15) demonstrated the feasibility of using laser-induced fluorescence (LIF) of boron oxide radicals in atmospheric pressure flames. A strong LIF signal was generated from the pumping of the ($00^0 0$ - $00^0 0$) transitions of the A-X system of BO_2. He was not successful in finding a LIF signal from the other important boron combustion intermediate, BO, in his brief search during his study of LIF of BO_2. Because of a rather limited tuning range of his laser, excitation bands for LIF of BO were severely limited. He faced a significant scattering from aerosols of solid boric acid from the reaction of BCl_3 with water vapor in the building air used in the flame.

III. Experimental Plan and Equipment

Objectives

The overall objective of this experiment is to demonstrate that the laser-induced fluorescence (LIF) technique can be used for determining the concentration of boron compounds in an atmospheric-pressure, boron seeded flame. Specific objectives included the optimization of LIF diagnostics of BO_2 as demonstrated by Schneider (15) and investigation of feasibility of LIF detection of BO. These two molecular species are thought to be the two most important reaction intermediates in the boron oxidation process.

Approach

This research was conducted in three phases. During the first phase, operation of the burner system and data collection system was optimized. By exciting the ($00^0 0$-$00^0 0$) transition band of BO_2 with band heads at 5456 Å and 5470 Å, good LIF spectra from the ($00^0 0$-$10^0 0$) transition for R1, 5790 Å and for R2, 5813 Å were obtained. These spectra agreed with the results of Schneider (15).

During the second phase, finding the optimum band for BO_2 LIF experiment was attempted. From several bands, the ($10^0 0$-$00^0 0$) band was excited and compared with the results of the first phase ($00^0 0$-$00^0 0$ band).

During the third phase, a LIF spectrum from BO was attempted. Liszt and Smith (16) have reported Frank-Condon factors $q_{v'v''}$ for the A-X system of BO. Since the Frank-Condon factor indicates the relative strength of the transition, with the higher Frank-Condon factor being the more probable transition, LIF signals from the bands which have the higher Frank-Condon factor than the others was observed.

Equipment Description

Figure 1 is a schematic diagram of the experimental system used in this research. The system is substantially the same as that used by Schneider (15:29).

Burner and Gas Supply System

The burner consisted of a cylindrical chamber and a bundle of capillary tubes. The chamber is at the base of the capillary tubes and is 4.5 cm in diameter and 2 cm in height. It is used for premixing the gases. As seen in Figure 1, the CH_4 and dry air/O_2 flow through tubes which are positioned tangentially to the chamber and in opposite directions. The BCl_3 flows directly into the chamber. This gives rise to a swirling of the gases and resulting in good mixing.

At the top of the burner, there is a bundle of sixty-one 1 mm diameter stainless steel capillary tubes brazed together to

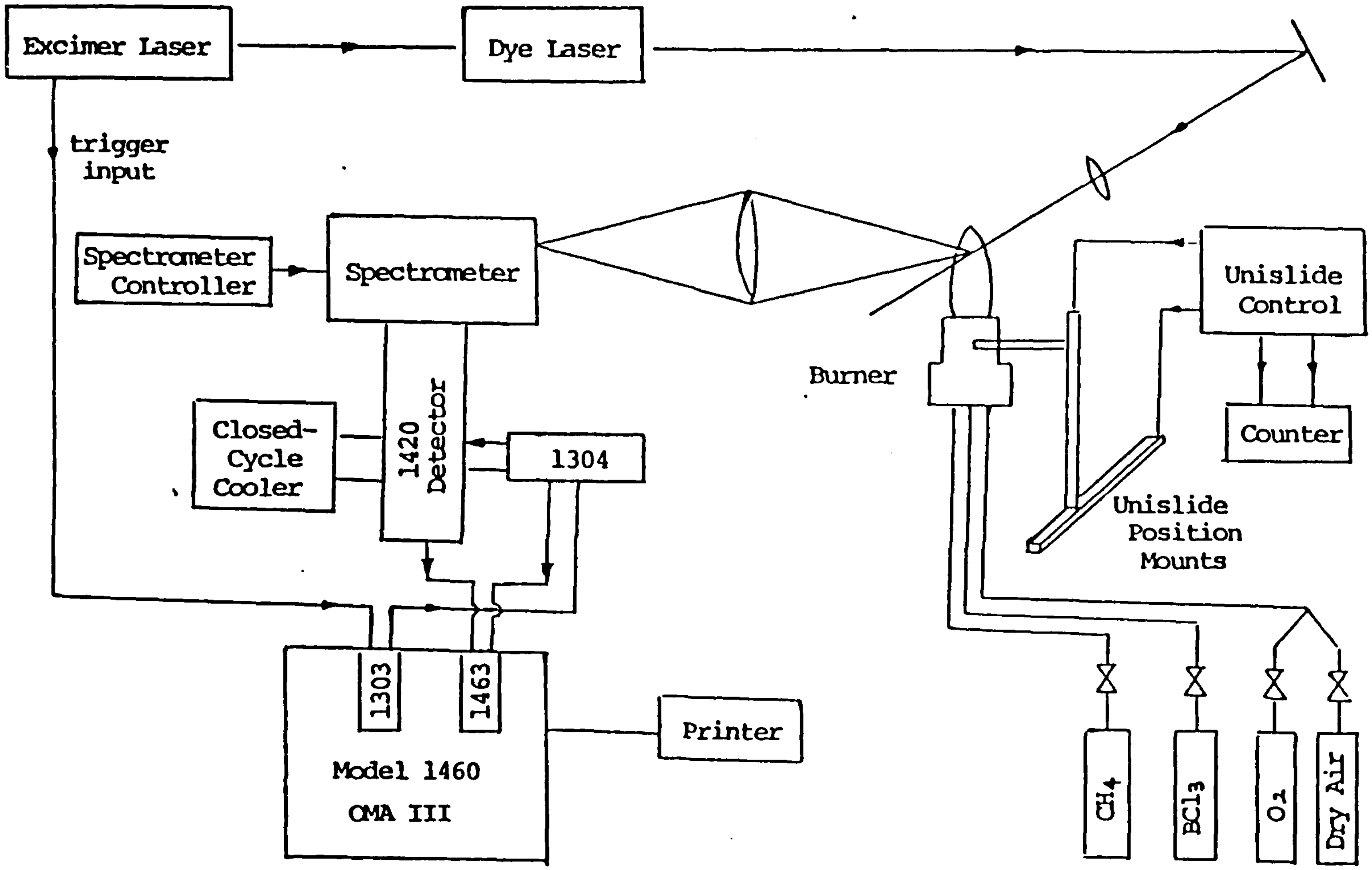


Figure 1. Schematic Diagram of Experimental Layout and Electronic Connections

form a core approximately 1 cm in diameter. The premixed gases flow through the core bundle which supports the flame.

Gas flow was regulated by four flowmeters. First, the dry air flowed and then the methane (CH_4) was added. This dry air was used throughout this experiment to avoid the scattering problems Schneider faced (15). After ignition by using a match, the flowrates were readjusted to maintain a stable blue flame without a yellow colored portion. The yellow color in the flame indicates incomplete combustion of carbon.

The typical height of the flame was around 6.5 cm tall. It was very hard to prevent fluctuations of the flame. If the flowrate of the dry air was increased, the flame fluctuated. If decreased, the yellow colored spot appeared. In addition, decreasing the methane gas flowrate brought a reduction in flame size. Paradoxically, this limited regime over which a stable flame could be maintained yielded reproducible results for each experimental session.

After achieving conditions for the flame stable, oxygen was added to the gas flow to form an inner flame cone which was approximately 2.5 cm tall. The inner flame cone propagated back down the capillary bundle even with a small excess in O_2 flowrate. Then BCl_3 was added to the flame and the color of the flame changed from blue to a green color. If flowrate of BCl_3 was increased, LIF signals also increased. However, that produced an annoying problem; the excessive BCl_3 gas made the hood over the burner corrode. Fortunately, the excessive flow rate could be easily detected by eye, since it produced a white smoke surrounding the flame.

A white colored powder was formed around the edge of the capillary tubes after several minutes of operation. Schneider mentioned this crystalline powder before, and identified it as H_3BO_3 (15:62). After approximately 1 1/2 or 2 hours of each burning process, the water soluble powder was cleaned off with distilled water.

As shown in Figure 1, a motorized Unislide Model B2500 translation stages were used to move the burner along the vertical and horizontal, laser beam, axis. Movement of the burner along the detection axis which is perpendicular to the laser beam axis was done by tilting the mirror and readjusting the focusing lens. This position along the third direction was adjusted while setting up and optimizing the optical alignment, then remained fixed during the remainder of the experiment. The translation stages were controlled with a Unislide Model 8202 M1 stepping Motor Controller, having a resolution of 5 microns and monitored with an integral position encoder.

Lasers

A pulsed dye laser (Lambda Physik FL 3002E) was pumped by a Lambda Physik Model EMG-101 MSC Excimer Laser. The excimer laser used XeCl excimer gas. During operation, the excimer laser used gas concentrations of Xe (80 mbar), He/HCl (100 mbar), and Ne (2420 mbar). It produced a 308 nm UV laser beam and 150 mJ output energy using a 22 kV power supply unit. The maximum repetition rate was 25 pps, but was usually operated at 20 pps. A gradual reduction of the excimer laser output power was observed. Subsequently, the output was monitored and compensated by increasing the power supply voltage from 17 kV upto 22 kV in order to maintain constant output. The lasing threshold was 14.5 kV, but operation at the higher voltage of 17 kV was recommended for safe operation and stable output. There was also a power loss from the dye laser, but the usable life of the dye solution is usually much longer than that of the excimer laser gas mixture. After approximately 10 hours of operation, it was refilled with a new batch of gases. The excimer laser provided a synchronized trigger signal to the data collection system as described in a separate section later in this chapter.

The dye laser, pumped by the excimer laser, provided a tunable output over a broad spectral range. By changing the dye solution, the dye laser could cover almost all wavelengths from the UV to near-IR. In this experiment, Coumarin 540A (517 - 612 nm), Bis-MSB (411 - 431 nm), DMQ (346 - 377 nm), Stilbene 420 (412 - 435 nm), and Coumarin 503 (479 - 562 nm) were used as dye solutions. When changing the dye solution, the dye circulator should be flushed very carefully. The dye circulators were rinsed with pure solvent several times until the rinsing solvent was no longer stained. This cleaning work was very important when switching from a "red" to a "blue" dye, since the absorption band of a dye solution is located in a shorter wavelength region than the fluorescence band. When changing the dye solution, the mirrors shown in Figure 1 also had to be changed to reestablish appropriate reflectivity characteristics.

When the power supply voltage for the excimer laser was changed from 17 kV to 22 kV, as mentioned before, the output energies of the dye laser varied anywhere from 10 mJ to 21 mJ (however, it differed for each dye solution and wavelength).

The laser beam was focussed on the flame with a lens having a focal length of 150 mm. The portion of the laser beam where the flame was located was about 4 mm in diameter.

Detection System

A PARC Model Optical Multichannel Analyzer (OMA III series) was used. It is a microprocessor controlled instrument that stores and displays spectral and related data curves. The most common application of this analyzer is its use as a computer controlled instrument for spectroscopy investigations. The hardware components of the detection system were a spectrograph, a detector, the detector controller, and the 1460 System Processor and its software.

The Model 1460 System Processor manages all of the functions of the system including data acquisition, manipulation (such as background subtraction and source compensation), display on its own CRT or plotting on an external plotter, and data storage on floppy disks. The processor sends instructions to the detector controller to manage the data acquisition process and receives digital output from the detector controller. Its software provides the functions necessary for data acquisition, manipulation, display, and storage. With a programming ability in BASIC, it is easy to use.

An Instruments SA, Inc. Model HR-640 0.64 m spectrometer was used for a spectral dispersion. It had a 1200 g/mm grating. The spectral calibration was done by using Oriel mercury discharge lamp with atomic lines in the region of interest.

A PARC Model 1420R-512-G Solid State Detector was used for detecting the optical signals. This model is an intensified silicon photodiode array detector which has 512 diodes and a microchannel plate to intensify the signal. For the LIF experiment, the gating mode was used rather than the continuous mode (CW). This detector was sensitive while the gate is "open". By gating the detector, the amount of flame chemiluminescence which contributed to the background was reduced. To reduce the "dark" counts originating from thermal electrons in the detector, the detector was cooled to -30°C with its own thermoelectric cooler. Before and during this cooling work, dry gas (nitrogen) was applied to the detector to keep the interior free of atmospheric moisture. But at least 30 minutes was required for background equilibration after the temperature lock signal was indicated on the OMA screen. After the detector stabilized thermally, a background count was collected without a

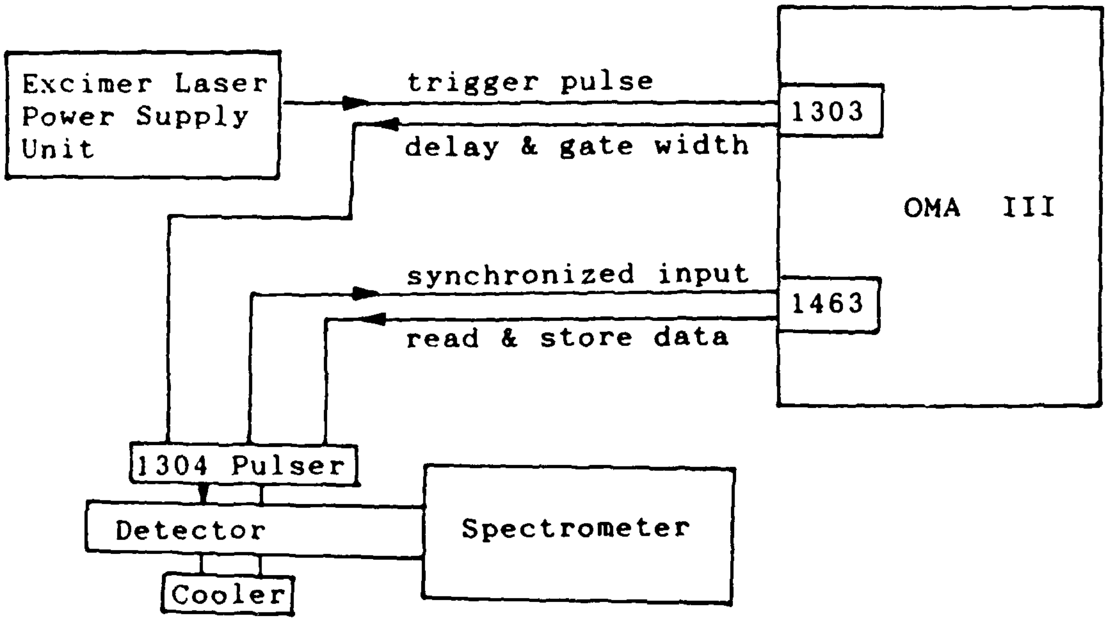
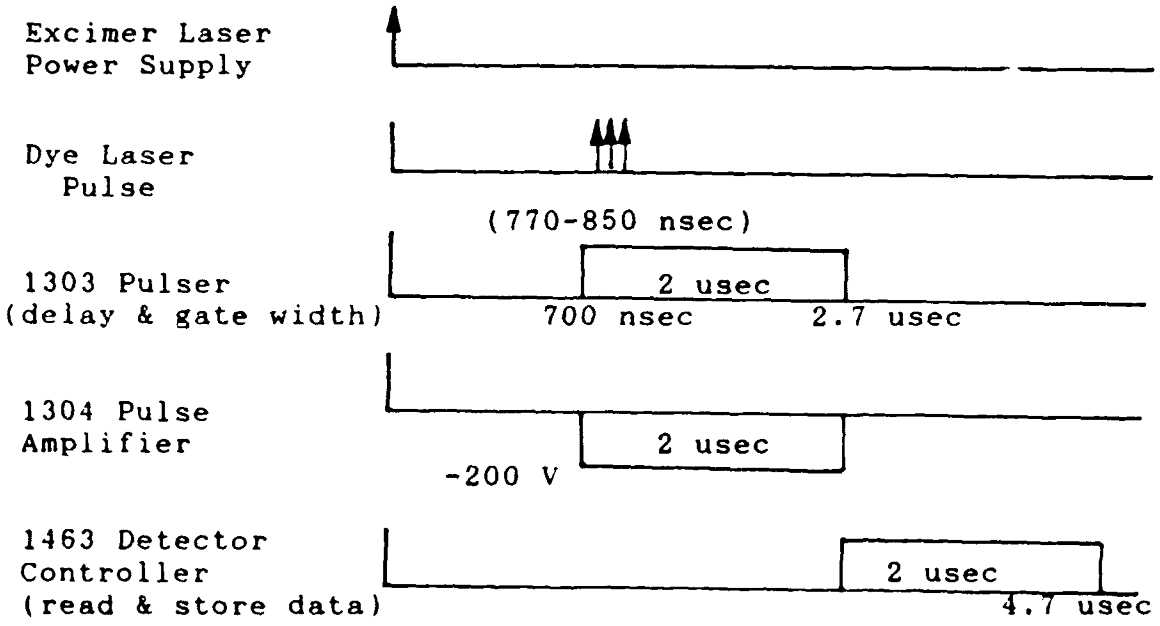


Figure 2. Schematic Diagram of the Data Acquisition Process



* 10 usec of gate width instead 2 usec was used during BO LIF survey due to a longer lifetime.
(BO$_2$: approximately 100 nsec
BO : approximately 1.7 usec)

* 2 usec gate width of the 1463 detector was fixed.

Figure 3. Timing Schedule

laser beam and stored for use in the background substraction.

Timing Schedule

The synchronous (sync.) signal of the excimer laser power supply provided the necessary trigger pulses to control the gate pulse generation and the scanning of the diode array. Figure 2 is a system diagram of the data acquisition process and Figure 3 is the timing diagram. Since the excimer laser pulse had a prolonged trailing edge, the leading edge was used for the trigger source.

A PARC Model 1303 Pulse Amplifier was controlled from either the touch screen or the keyboard of the Model 1460 optical multichannel analyzer. The 1303 was triggered by the sync. pulse from the excimer laser. Through the OMA III software, delay and gate width for the detection timing were set and sent to a PARC Model 1304, acting as a second pulse amplifier. This 1304 accepts pulses from the 1303 and provides negative-going 200 V output pulses which control the bias voltage between the photocathode and the microchannel plate, thus intensifying the signals. The 1304 applies the gate controlling pulses to the Model 1420 detector. The trigger output pulse, which has a fixed width of 2 us, was sent to the 1463 Detector Controller to "read" the signal on the diodes and "store" the data in memory. This "read" and "store" sequence was coincident with a trailing edge of the gate pulse.

The time between these pulses could be adjusted over a wide range. As shown in Figure 3, the total data acquisition time is 12.7 us for a 10 us gate width. With the 20 pps repetition rate of the laser, there is no problem in time sequencing.

One interesting observation was the dependence of the time delay between the sync. pulse and laser pulse on the supply voltage. As the supply voltage increased from 17 kV to 22 kV, the delay time of the laser beam, measured by Rayleigh scattering, decreased from 850 nsec to 770 nsec. Setting the delay time to 700 nsec covered the laser beam pulse width and could catch the immediate LIF signals from the flame.

IV. Laser-Induced Fluorescence of BO_2

LIF of BO_2

Schneider (15) demonstrated nonresonance LIF of BO_2 with the excitation of the (00^00-00^00) band and detection of fluorescence at the (00^00-10^00) band. Although this particular combination of bands was found to be excellent for diagnostic application, it was by no means clear if this was the best combination. For this reason, it was decided to survey all the excitation and fluorescence and fluorescence bands to identify the best pair of bands for LIF diagnostics of BO_2 in flame.

According to Clyne and Heaven, the 434 nm band of BO_2 was extremely intense in their LIF studies, being approximately comparable to I_2 or Br_2 in intensity (17:305). This intense band was readily identified as the (00^02-00^00) transition of BO_2 A-X, by comparison with the tabulated absorption data of Johns (18:1748). Huie et al., had previously thought mistakenly this band to be due to the BO radicals (19:405). But, Clyne and Heaven corrected that assignment to be the BO_2 band (17:304).

For exciting this band, the dye was changed to Stilbene 420 (lases in 412 - 435 nm) which had a maximum lasing wavelength at 435 nm. With the detection system used in this experiment, approximately a 140 Å wavelength range could be covered at a time. To cover all possible wavelengths and some overlap between subsequent steps, the spectrometer was tuned from 4000 Å to 6400 Å in steps of 100 Å. Data collection was concentrated on wavelengths longer than the excitation wavelength. Mostly, the portion of the flame just above the inner cone was investigated, since preliminary work indicated that the BO_2 signal was most intense there.

According to Hodgson (20), the radiative lifetime of the first excited state ($A^2\Pi_u$) 00^02 is almost the same as that for the other states (Table II).

TABLE II

Transition Probabilities for the $A^2\ _u$ State of BO_2 (20)

State	Radiative Lifetime (nsec)	A Coeff. (10^7 sec^{-1})	
00^00 $^2\Pi$	91 ± 4	1.1	
10^00 $^2\Pi_{1/2}$	94.8 ± 1.6	1.05	
10^00 $^2\Pi_{3/2}$	91.6 ± 3.8	1.09	
11^10 $^2\Sigma^+_{1/2}$	91.4 ± 3.6	1.09	
11^10 $^2\Sigma^+_{3/2}$	110 ± 2	0.91	
11^10 $^2\Delta_{3/2}$	102 ± 12	0.98	
11^10 $^2\Delta_{5/2}$	101 ± 2	0.99	
20^00 $^2\Pi_{3/2}$	98.5 ± 0.6	1.02	
20^00 $^2\Pi_{1/2}$	101.6 ± 1.4	0.98	
20^00 $^2\Pi_{3/2}$	103.8 ± 1.4	0.96	^{10}B
02^20 $^2\Pi_{3/2}$	89.3 ± 3.8	1.12	
02^00 $^2\Pi_{1/2}$	97.1 ± 4.2	1.03	
02^00 $^2\Pi_{3/2}$	103 ± 4	0.97	
12^00 $^2\Pi_{3/2}$	101.3 ± 2.8	0.99	
12^00 $^2\Pi_{1/2}$	124 ± 2	0.81	
12^00 $^2\Pi_{3/2}$	103 ± 0.8	0.97	^{10}B
12^00 $^2\Pi_{1/2}$	96.2 ± 2	1.04	^{10}B
00^02 $^2\Pi_{3/2}$	105 ± 6	0.95	
00^02 $^2\Pi_{1/2}$	121 ± 6	0.83	

But, more recent work on the radiative lifetime of BO_2 $A^2\Pi$ by Clyne and Heaven showed the 00^02 state was rapidly quenched (the reason was not explained), while the 00^00 or 10^00 states were not

(17:309). The most probable reason for not finding LIF signals from the (00^02-00^00) excitation is thought to be heavy quenching by the high pressure environment. As mentioned earlier, their experimental pressure was 0.3-1.15 torr instead of 760 torr of the present experiment.

Based on the assumption that the lowest vibrational level has the greatest population, the (10^00-00^00) band was chosen for excitation. With the Coumarin 540A, both the (00^00-00^00) band (R1;5456.4 Å, R2;5471 Å) and the (10^00-00^00) band (R1;5169.5 Å, R2;5181.5 Å) could be pumped. But, since the (10^00-00^00) band was located in the wing of the dye efficiency curve (517-612 nm), output energy was as low as 1.5 mJ. Coumarin 503 dye was selected for the (10^00-00^00) band of BO_2 instead, and its solution was filled in a second dye circulator. So, by simply changing the dye circulators, LIF characteristics from both bands could be compared against each other.

Figure 4 is an example of the fluorescence spectra obtained. In this case, the pump band for the upper spectrum was the R1 band of the (10^00-00^00) transition at 5169.5 Å and the lower spectrum was the R2 transition at 5181.5 Å. Comparison of the two spectra shows the difference between the two excitation schemes. The strongest band observed in the upper spectrum is the R1 band of the (10^00-10^00) transition and that in the lower is the R2 band. This flame operating at a relatively high pressure of 760 torr, should induced considerable collisional mixing. As a result, other bands also appeared in addition to

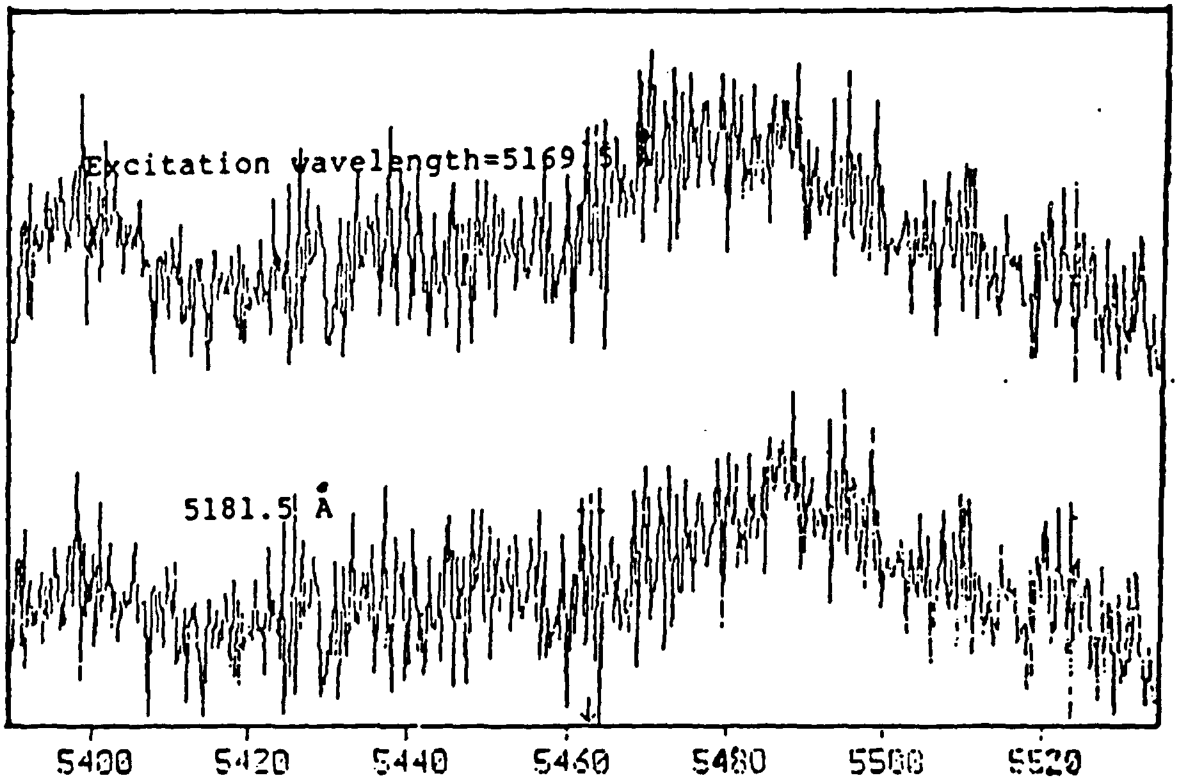


Figure 4. Comparison of the fluorescence spectra

The upper: the R1 band excitation of the 10^00-00^00 transition at 5169.5 Å

The lower: the R2 band excitation at 5181.5 Å the pumped band.

For the purpose of background compensation, a spectrum was collected with the laser beam blocked and stored as a representative background spectrum. Five hundred LIF spectra were accumulated, each of which was compensated for the background reading.

In the search for the best excitation band, the portion of the flame just above the inner cone, 3 cm above the burner, was used. The spectrometer was fixed to the $(10^{0}0-10^{0}0)$ transition (5285 Å - 5535 Å), as the dye laser was scanned.

First, the dye laser was scanned over the range from 5163 Å to 5173 Å which covers the R1 band of the $(10^{0}0-00^{0}0)$ transition at 5168.84 Å. Figure 5 shows several excitation spectra. The best excitation wavelength in this case was determined to be 5169.5 Å. Figure 6 shows an expanded fluorescence spectrum with a 5169.5 Å excitation.

Next, the dye laser was tuned across the R2 band of the $(10^{0}0-00^{0}0)$ transition at 5180.74 Å. It scanned from 5175 Å to 5186.5 Å. Figure 7 shows several fluorescence spectra obtained. Among these, the most intensive signals occurred at an excitation wavelength of 5181.5 Å. Figure 8 shows an expanded spectra for this case.

After determining the best excitation band, 5169.5 Å for the R1 band and 5181.5 Å for the R2 band, the fluorescence scan was observed from 4010 Å to 6540 Å in 100 Å steps, which made observation ranges overlap. These fluorescence scans were

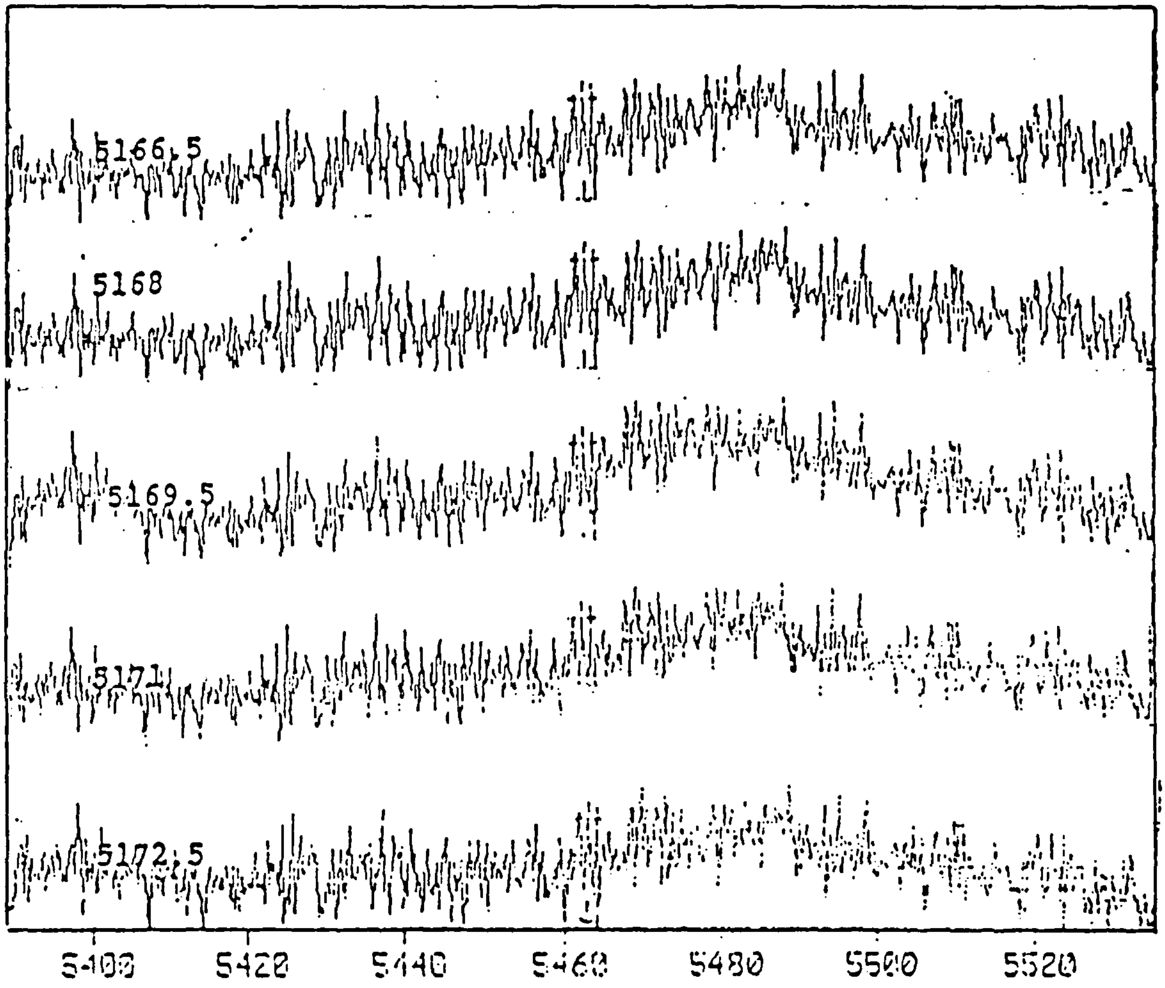


Figure 5. Excitation scans at different laser wavelengths around the R1 band of the (10^00-00^00) transition

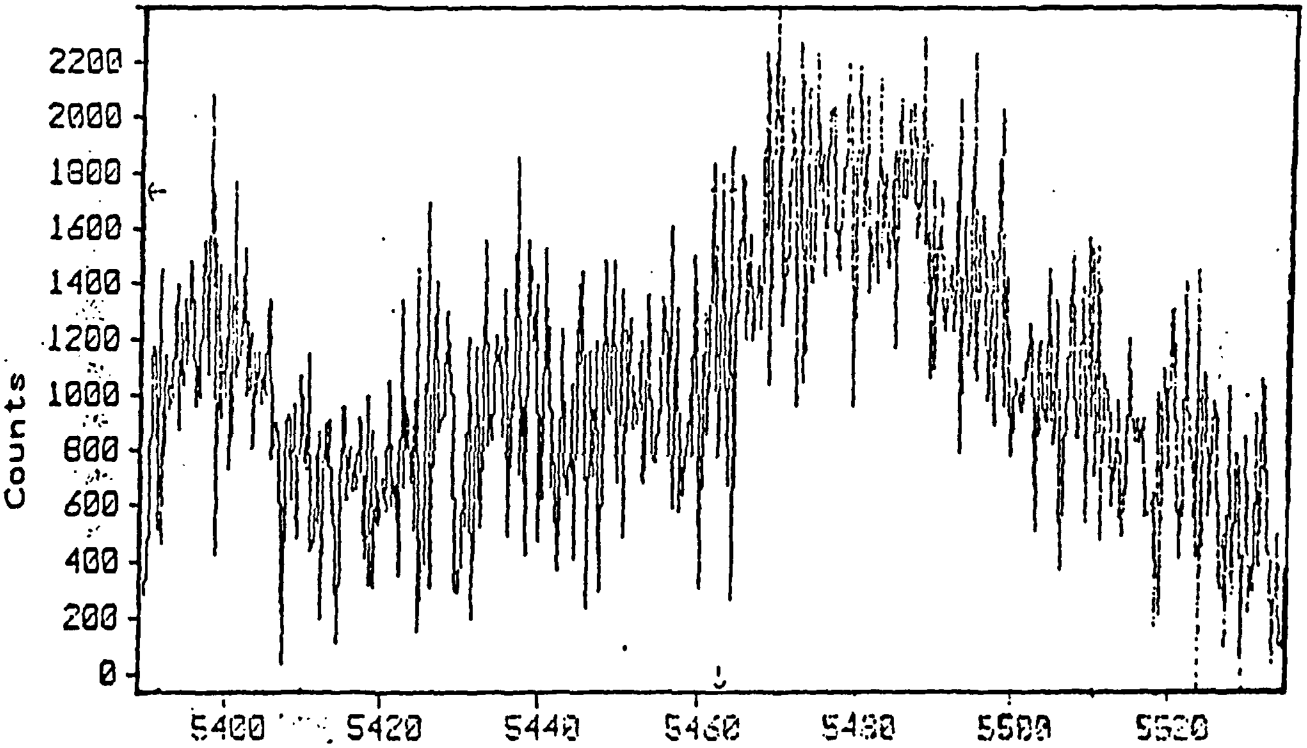


Figure 6. Excitation scan, laser wavelength at 5169.5 Å

made at both the R1 band of 5169.5 Å and the R2 band of 5181.5 Å. Data from R2 band excitation are shown in Appendix A. There were several prominent bands observed at wavelengths longer than the excitation wavelength, and these are listed in Table III.

TABLE III

LIF Bands Observed

Wavelength (Å)	Band
6401.8	Not Assigned
6396.2	$00^{0}0$-$00^{0}2$ R2
6377	$00^{0}0$-$00^{0}2$ R1
5842.3	Not Assigned
5831.3	$10^{0}0$-$20^{0}0$ R2
5813.1	$00^{0}0$-$10^{0}0$ R2
5804.9	$10^{0}0$-$20^{0}0$ R1
5486.8	$10^{0}0$-$10^{0}0$ R2
5469.4	$10^{0}0$-$10^{0}0$ R1

There were two regions which showed a considerable amount of LIF signals around 5480 Å (for the $10^{0}0$-$10^{0}0$ band) and around 5800 Å (for the $10^{0}0$-$20^{0}0$ band). Between the two fluorescent bands, however, the ($10^{0}0$-$20^{0}0$) band was more prominent. So, this band was used for comparison with the ($00^{0}0$-$00^{0}0$) band excitation. Fortunately, the ($00^{0}0$-$10^{0}0$) band which resulted

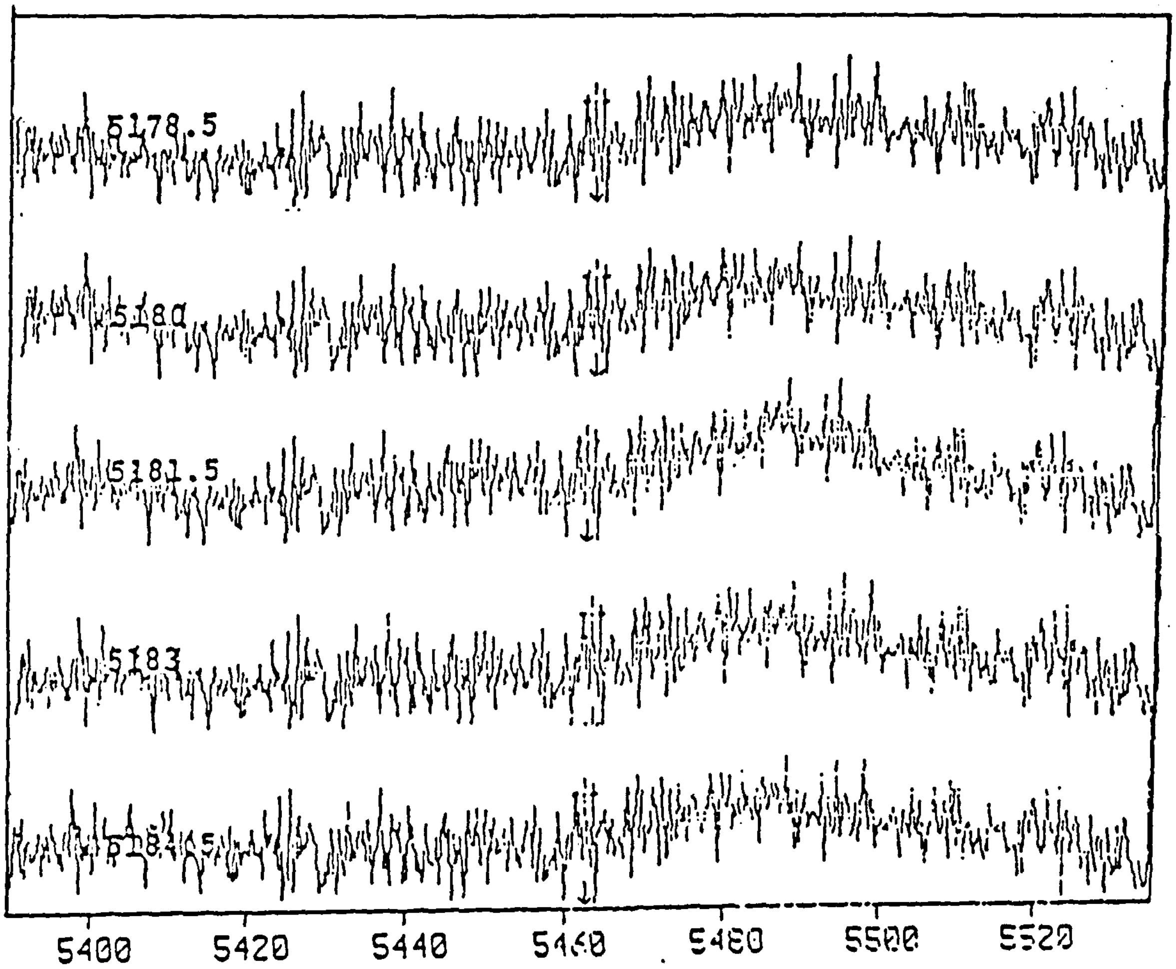


Figure 7. Excitation scans at different laser wavelengths around the R2 band of the $(10^{0}0\text{-}00^{0}0)$ transition

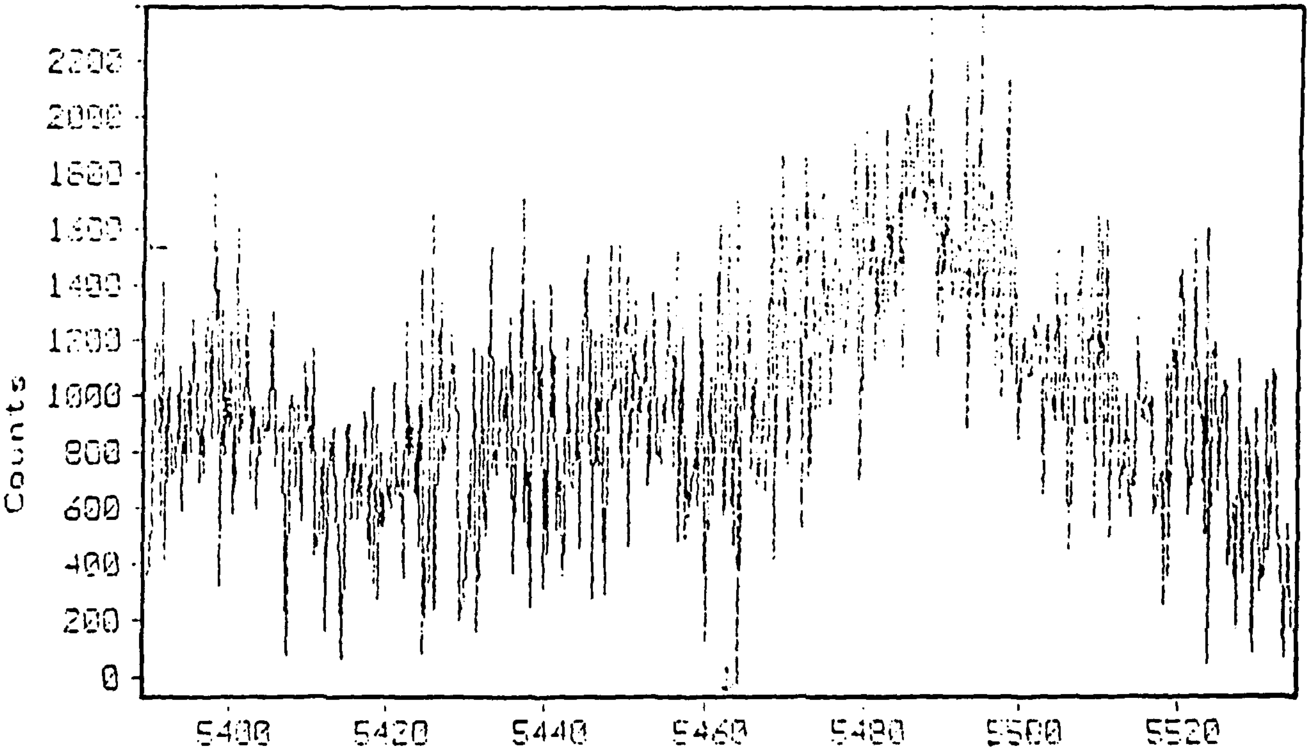


Figure 8. Excitation scan, laser wavelength at 5481.5 Å

from exciting the (00^00-00^00) band was located in the same wavelength range as the (10^00-20^00) band which resulted from exciting the (10^00-00^00) band.

Comparison of excitation bands

To determine the best bands for LIF diagnostics of BO_2, all parameters which affect the LIF signals should be examined.

Since the strongest fluorescence bands with the two excitation bands were located in the same spectral region, the spectrometer was set for the region from 5735 Å to 5880 Å. To keep the changing flame conditions from affecting the LIF signals, both bands were excited one after the other by simply changing the dye circulators, one with Coumarin 540A and the other with Coumarin 503. One of the most important parameters which was thought to affect the LIF signals was the output power of each laser beam. To determine the laser power dependence of the LIF signals (saturation effect), the output LIF counts for various energies were counted. The output LIF signals increased with energy increase. The results are shown in Figure 9.

Even with the highest energy of 21 mJ, no saturation in fluorescence signal was observed. Figure 9 shows a linear relationship between the laser beam energy and the LIF intensity. Therefore, the highest possible power was preferred. The maximum output energy from Coumarin 503 was 13 mJ with the 22 kV power source. To match both output energies, the power source

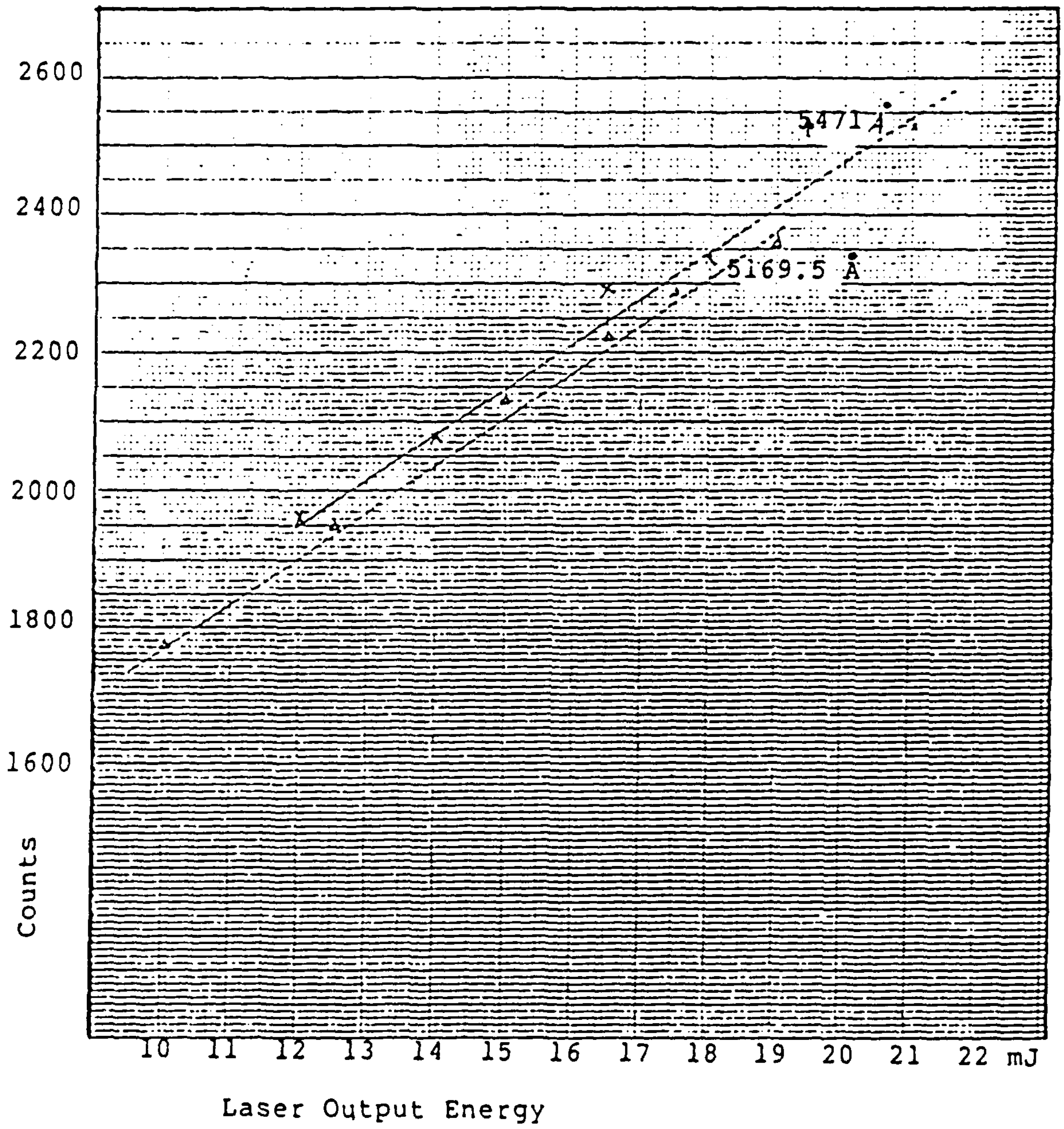


Figure 9. Relationship between laser output energy and LIF intensity

for Coumarin 540A was cut down to 18.5 kV. As mentioned earlier, the time delay depends on the supply voltage. But, setting it to 700 nsec was sufficient to place the laser pulses within the detector gate.

All the spectra obtained are collected in Appendix A and B. Figure 10 shows the strongest regions (5735 Å-5880 Å) from both bands. Each main peak was from the $(10^{0}0-00^{0}0)$ band excitation to the $(10^{0}0-20^{0}0)$ transition and from the $(00^{0}0-00^{0}0)$ band excitation to the $(00^{0}0-10^{0}0)$ transition.

From Figure 10, it can be seen that excitation of the R2 band of the $(10^{0}0-00^{0}0)$ transition has more prominent and intense peaks. (Note the signal counts, the $10^{0}0-00^{0}0$ excitation has approximately 0.4 times more counts at fluorescence peak.) From the overall fluorescence scan, it is further observed that exciting the R2 band of the $(10^{0}0-00^{0}0)$ transition produces more intense LIF signals. In addition to the region of the $(10^{0}0-20^{0}0)$ transition, the region of the $(10^{0}0-10^{0}0)$ transition also showed a considerable LIF signal (Figure 6 and 8).

Based on these observations, it can be stated that the excitation of the $(10^{0}0-00^{0}0)$ band followed by fluorescence detection of the $(10^{0}0-20^{0}0)$ is the optimum choice for diagnostics of BO_2 in flames.

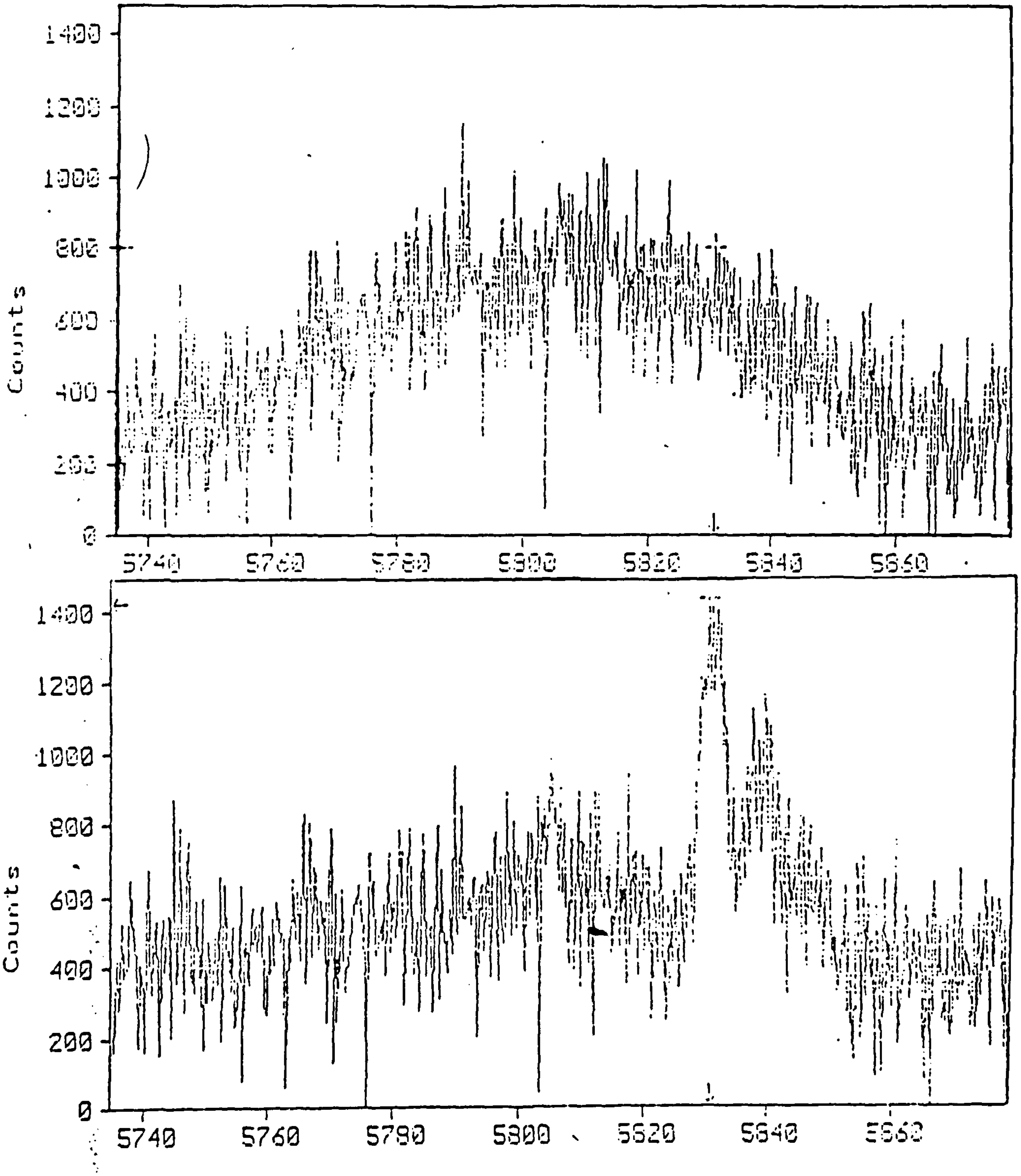


Figure 10. Comparison of fluorescence spectra between the (10^00-00^00) and (00^00-00^00) band excitations

The upper: the (00^00-00^00) band excitation at 5471 Å

The lower: the (10^00-00^00) band excitation at 5181.5 Å

V. Laser-Induced Fluorescence of BO

The feasibility of using LIF for the detection of BO in an atmospheric-pressure flame was not determined.

Described in the preceding section, excitation of LIF from BO_2 was readily achieved with Coumarin 540A dye. The ($00^0 0$-$00^0 0$) band of BO_2 was excited and showed good LIF characteristics. Since both the ($00^0 0$-$00^0 0$) band of BO_2 (5470 Å) and the (0-3) band of BO (5550 Å) could be excited with the same dye (5210 - 6050 Å), LIF experiment for BO was commenced using the same dye as for BO_2. According to Liszt and Smith, the (0-3) transition of BO has the highest Frank-Condon factor of any of those in the A-X system (16:1049). With excitation of the (0-3) band, the possible candidate fluorescence transitions were the (0-0), (0-1), (0-2), and (0-4) bands. These transitions had relatively high Frank-Condon factors except the (0-0) band. A survey for BO LIF signal was performed with the spectrometer centered at each band. After the spectrometer was tuned to the desired wavelength, the (0-3) band was excited in 0.5 Å steps from 5545 Å to 5555 Å. Various regions of the flame were searched, but no noticeable signal was obtained.

To be sure, the (0-3) band is not one of the best excitation bands owing to the fact that the thermal population of the v"=3 level is only a few percent even at the flame temperature. This suggested the (0-0) band as a possible candidate.

For pumping the (0-0) band of BO, the dye was changed to Bis-MSB which was shorter-lived than the others. Changing the wavelength required changing the beam steering mirrors. After changing mirrors, optical alignment was readjusted through a Rayleigh scattering zone caused by air molecule scattering. Moving out to longer wavelengths, the (0-1), (0-2), (0-3), and (0-4) fluorescence bands were searched. From these trials, no identifiable signal was detected.

After efforts to detect nonresonance fluorescence, the detection of the resonance LIF from the (0-0) band was attempted. Since the BO molecule had relatively long lifetime 1.78±.14 usec (17:306), the resonance LIF could be achieved by gating the detector to avoid the Rayleigh signal which occurs instantly.

TABLE IV

Transition Probabilities for the $A^2\Pi_i$ State of BO (17)

State (v')	Lifetime (usec)	A Coeff. (10^5 sec^{-1})
0	1.78 ± 0.14	5.62
4	1.94 ± 0.17	5.15
7	1.62 ± 0.02	6.17
9	1.86 ± 0.01	5.38
10	1.67 ± 0.13	5.99
11	1.66 ± 0.09	6.02
Average	1.7 ± 0.1	5.88

To avoid the Rayleigh scattering, various time delays of the 1303 pulse amplifier were tried (see Figure 3). As mentioned before on page 16, the time delays were dependent on the excimer laser discharge voltage. Since the excimer laser pulse shape has an extended trailing edge, counts for Rayleigh scattering were gradually decreasing with increasing delay time. Fortunately, that gradual decrease was of limited duration, approximately 350 nsec. This was much smaller than the BO lifetime. After setting the time when the Rayleigh scattering disappeared, resonance LIF was looked for. Even in this case, there was no identifiable signal.

In absorption, the most intense band was expected to be the (3-0) transition (3670 Å), for which the Frank-Condon factor is 0.1724 (16:1049). The dye was changed to DMQ (346-377 nm). With DMQ dye, the (4-0) band (3515 Å) could also be pumped. Its Frank-Condon factor is 0.1576. When pumping the (3-0) band, the probable fluorescence transitions are (3-9), (3-10), (3-11) which have higher Frank-Condon factors. But they are in IR range. The other bands, such as (3-2), (3-3), (3-5), (3-6), etc., were examined while changing the location of the laser beam in the flame. The (3-0) band, as well as the (4-0) band, didn't show any noticeable signals for LIF. It had to be concluded that the LIF of BO could not be detected under the present condition. The lack of results for BO LIF was disappointing.

There are some possible reasons for this failure. The first probable cause is quenching. Because of the long lifetime of the first excited level of BO (v'=0 level average lifetime is 1.78+0.14 usec, 17:306) which is almost 15 times longer than the BO_2 lifetime, the excited BO molecules would lose their energies by quenching. Especially, with an atmospheric pressure of 760 torr, there is much collisional interaction, thus quenching. The previous workers, Clyne and Heaven (17), Huie and others (19), did work at a total pressure of a few torr (Clyne: 0.3-1.15 torr, Huie: 0.05-1.2 torr). The effect of quenching can be minimized by saturating the excitation transition. To that end, the highest possible laser power is preferred. However, it must be remembered that even a 21 mJ of laser pulse energy in 8 nsec over a 0.5 cm^2 beam, representing a power density of 5 MW/cm^2, was not sufficient to saturate.

The second possible reason is the small concentration of BO molecules produced in the flame. Clyne and Heaven reported spectra of BO_2 radicals from the reaction of O_3P atoms with BCl_3 with O_2 present; No BO radicals were detected under these conditions. The source of BO radicals was the reaction of BCl_3 with a mixture of O_3P and N_4S atoms in the absence of O_2 (17:299). The flame used here was a reaction of BCl_3 with CH_4, O_2, and dry air. It is not clear how much BO would be present in the flame under our operating conditions. However, if one accepts the proposed reaction channels of Glassman (14) and King (1), BO is a precursor of BO_2. So, if BO_2 is present, then BO must also be present to some degree.

VI. Conclusion

As a part of research into the combustion of boron in air, this research investigated the laser-induced fluorescence (LIF) as an in-situ probe for boron oxides (BO_2 and BO) in boron-seeded atmospheric-pressure flames.

A search was conducted for the best excitation band for the BO_2 LIF experiment. Among several excitation bands, the (00^00-00^00) band and the (10^00-00^00) band were chosen based on both previous LIF work and our own preliminary survey. These two bands were examined in further detail. The excitation of the (10^00-00^00) band followed by fluorescence detection of the (10^00-20^00) was the optimum choice for diagnostics of BO_2 in flames.

A rather extensive search for LIF signal of BO was conducted. Unfortunately, no LIF signal attributed to BO was detected. One possible reason for this negative result is a heavy quenching of BO under a high-pressure environment. Note that all previous observation of LIF of BO were achieved in the very low pressure, usually around 1 torr. Perhaps the BO concentration in our flame is too low to be detected with the present system. Even then, it is hard to accept this possibility since the boron oxidation starts from the formation of BO, it must be present to some degree. This point needs to be explored further.

Appendix A: Laser-Induced Fluorescence Survey Spectra

The following figures illustrate the laser-induced fluorescence produced with exciting the R2 band of the $(10^{0}0-00^{0}0)$ transition of BO_2 in the atmospheric pressure flame:

Mix: CH_4/Dry Air/O_2/BCl_3

Pump: 5181.5 Å, 13 mJ per pulse

Spectrometer Slits: 200 microns

Scans: 200

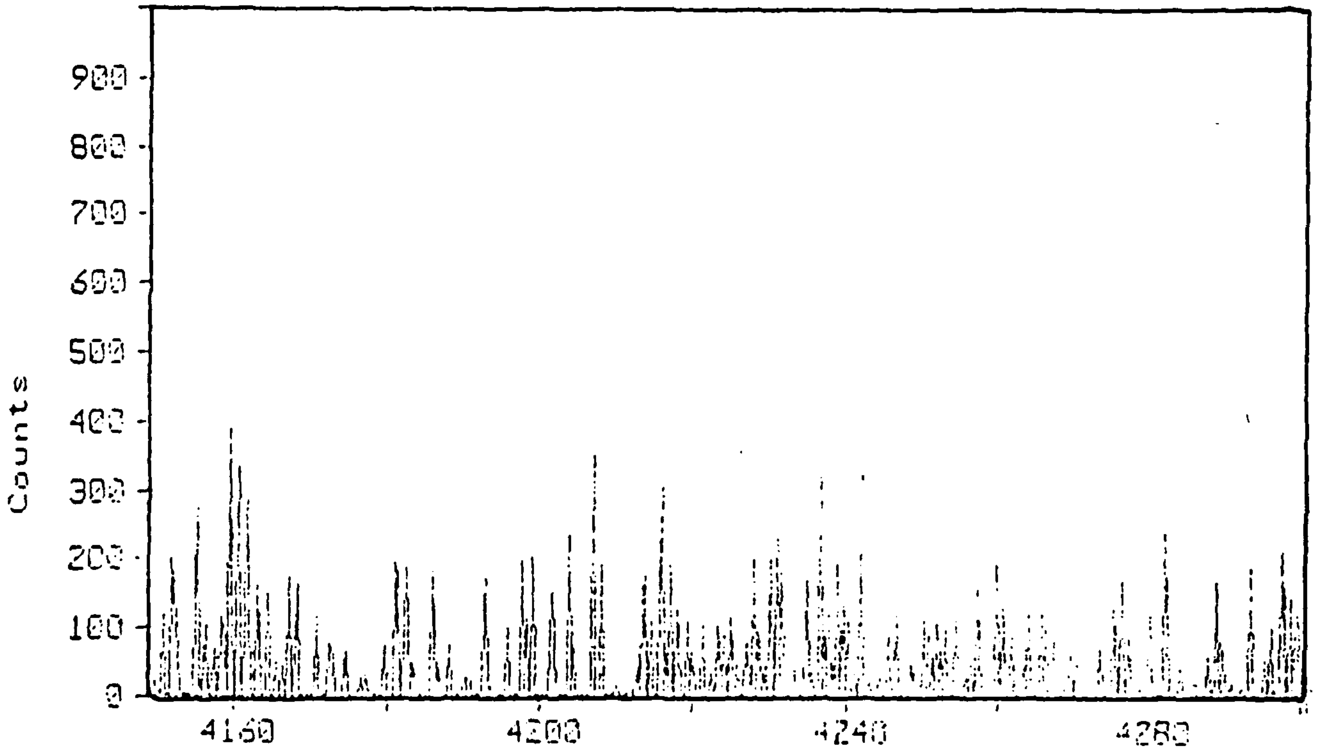


Figure 11. Induced Fluorescence (Laser at 5181.5 Å), 4150-4300 Å

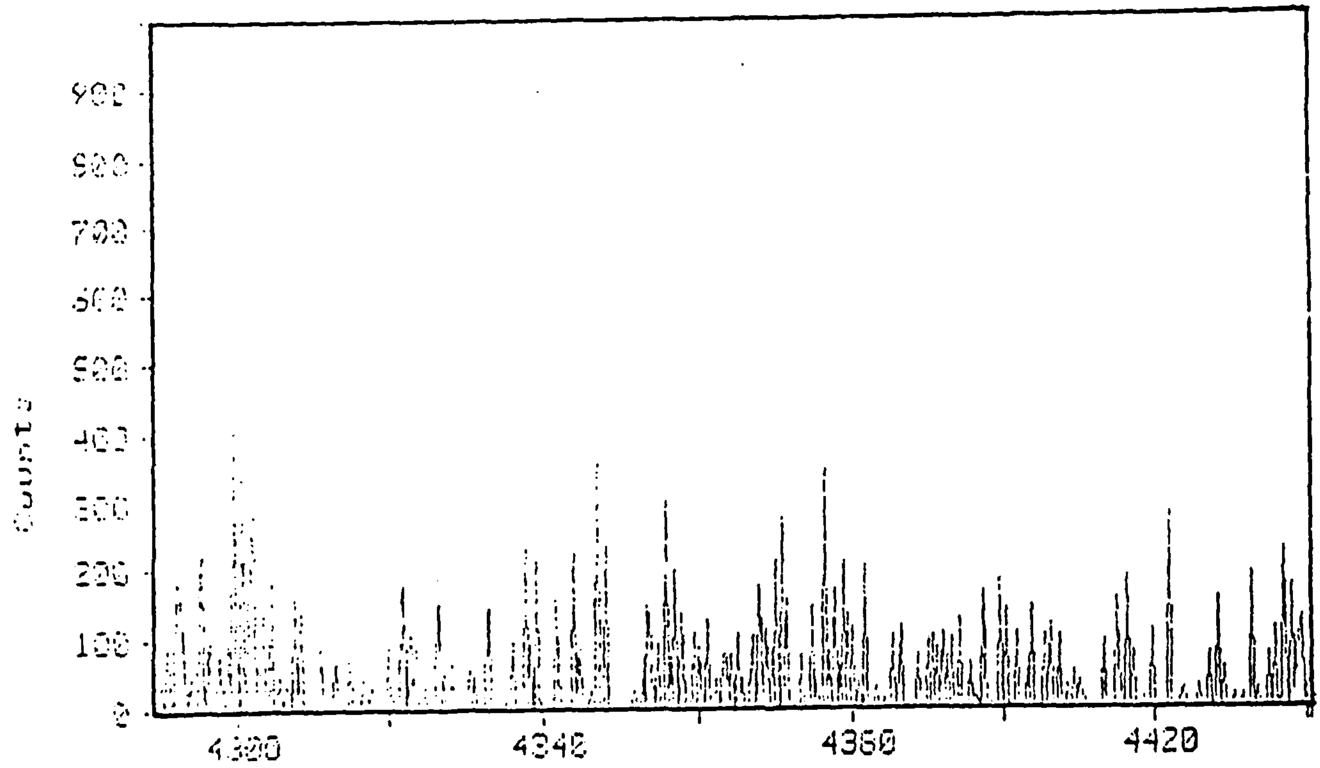


Figure 12. Induced Fluorescence (Laser at 5181.5 Å), 4290-4440 Å

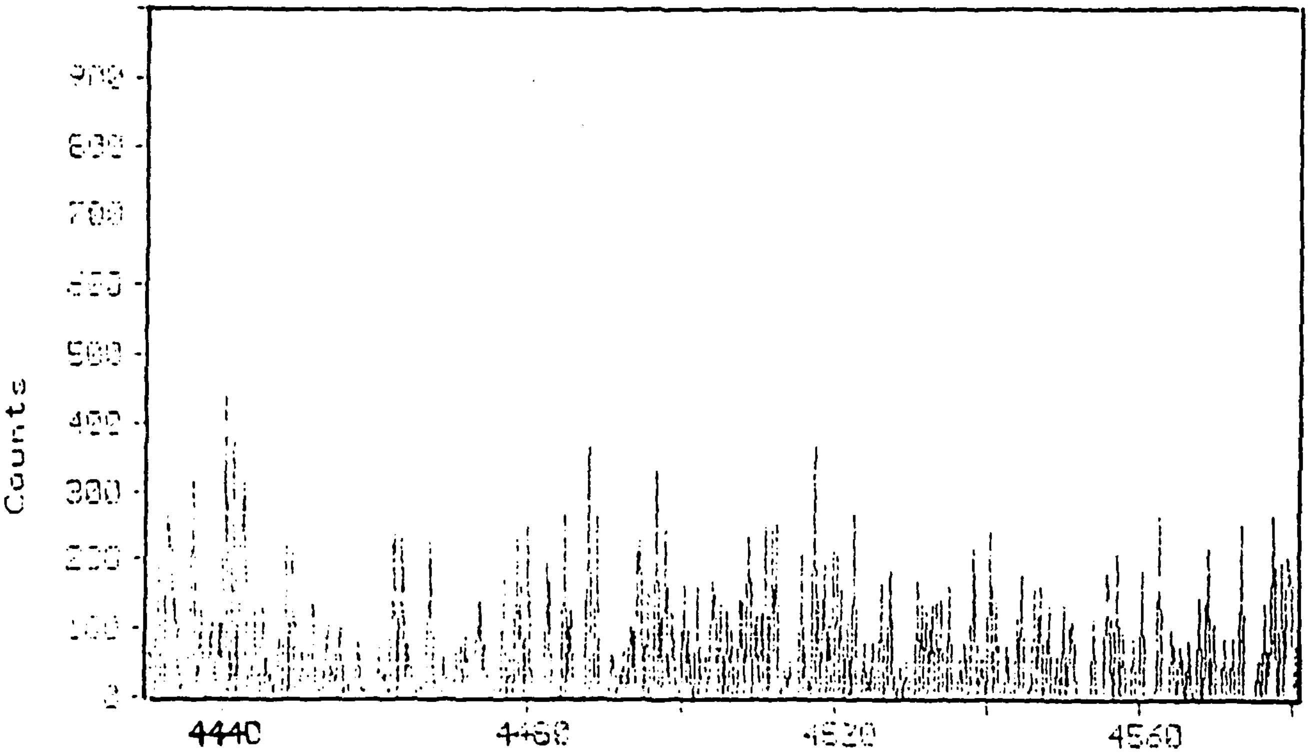


Figure 13. Induced Fluorescence (Laser at 5181.5 Å), 4430-4580 Å

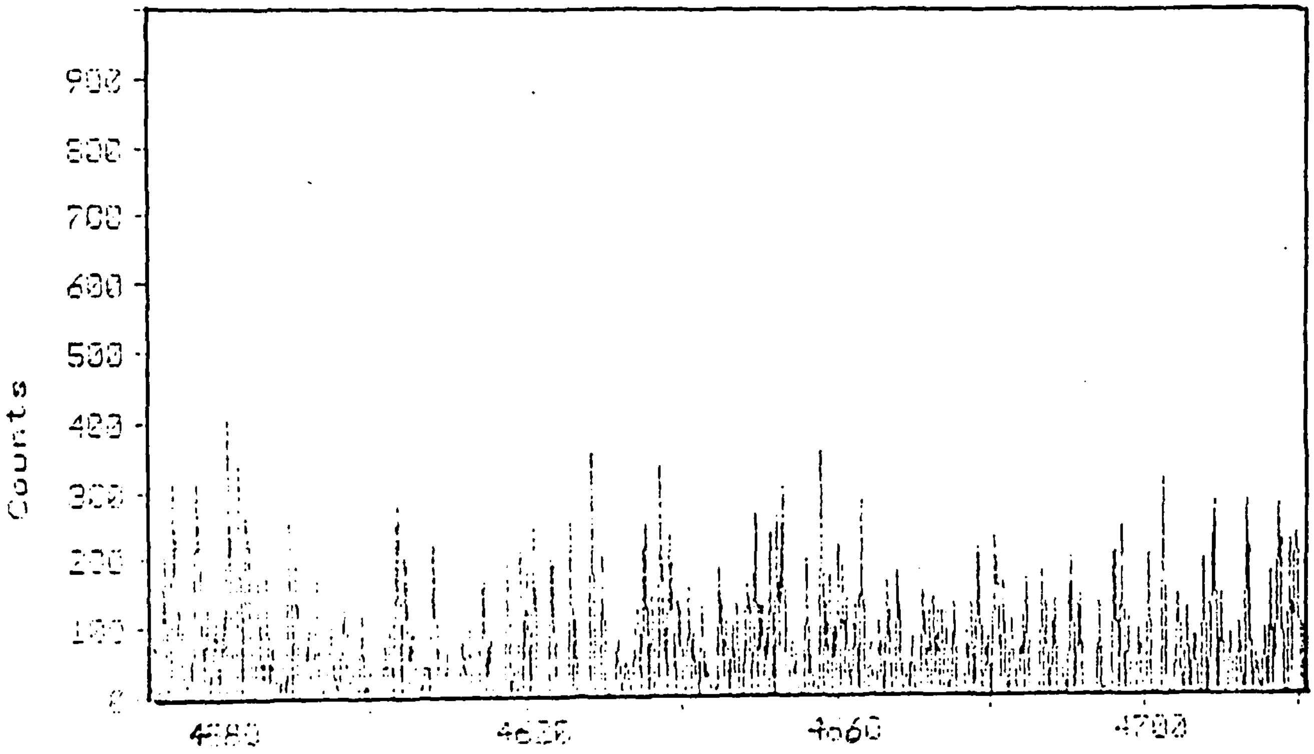


Figure 14. Induced Fluorescence (Laser at 5181.5 Å), 4570-4720 Å

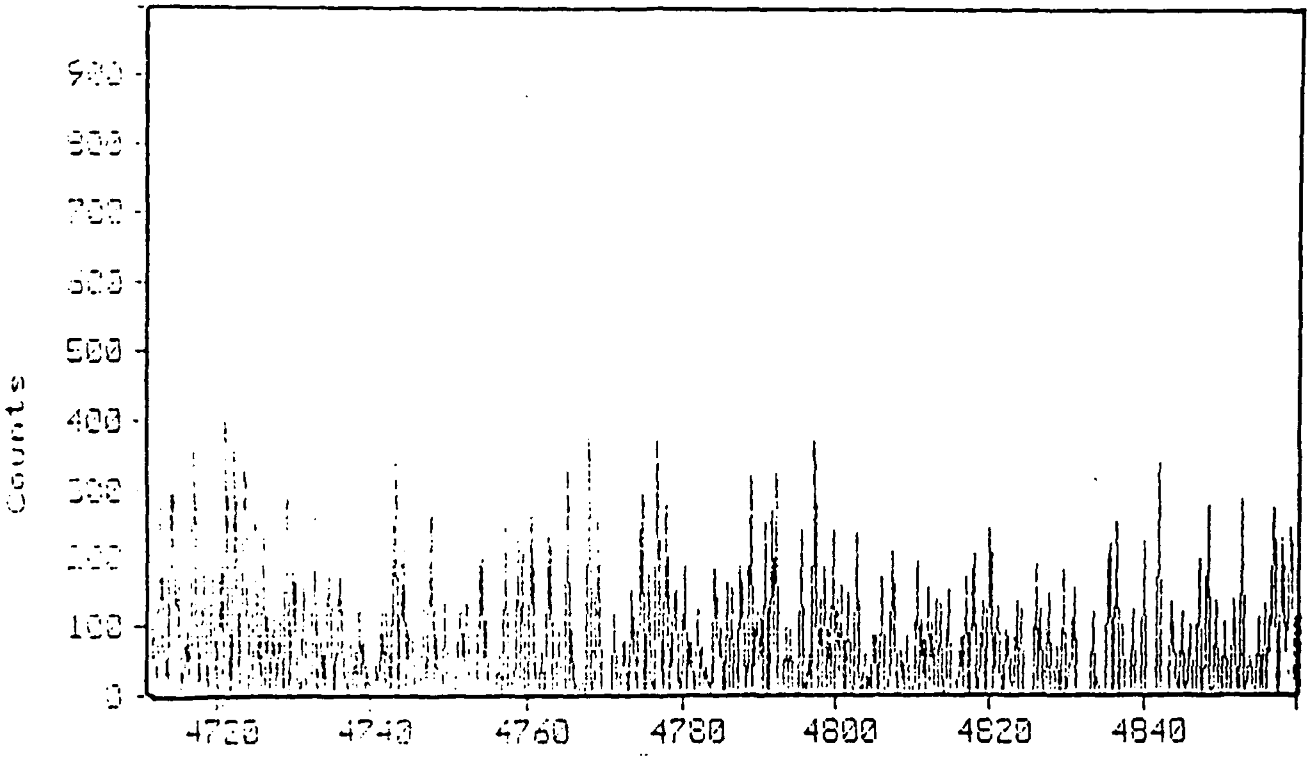


Figure 15. Induced Fluorescence (Laser at 5181.5 Å), 4710-4860 Å

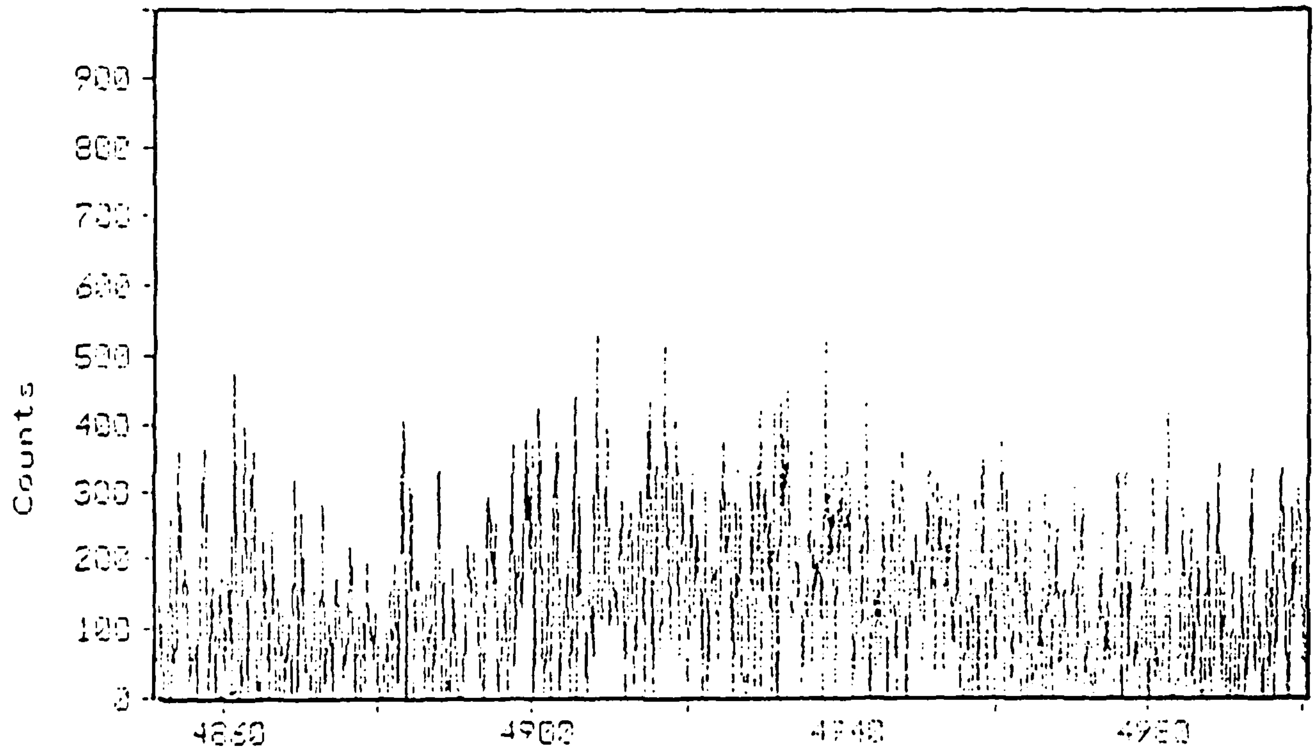


Figure 16. Induced Fluorescence (Laser at 5181.5 Å), 4850-5000 Å

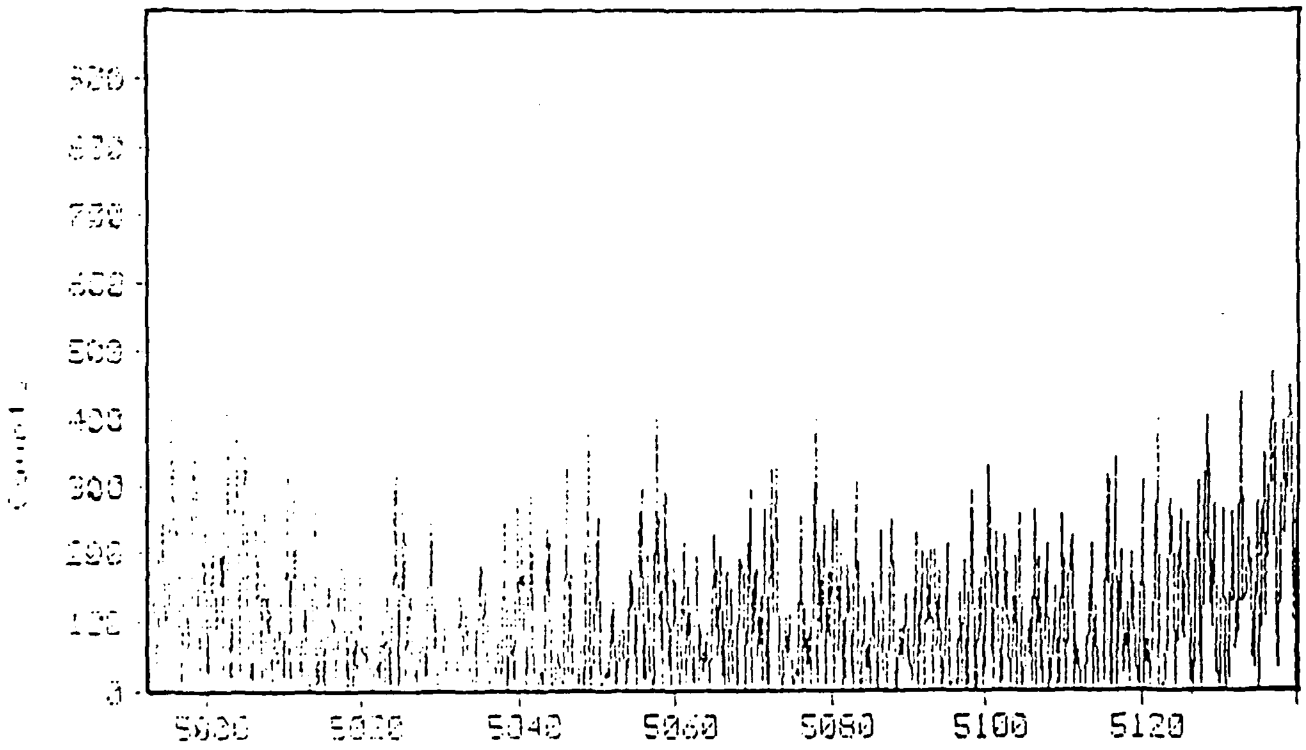


Figure 17. Induced Fluorescence (Laser at 5181.5 Å), 4990-5140 Å

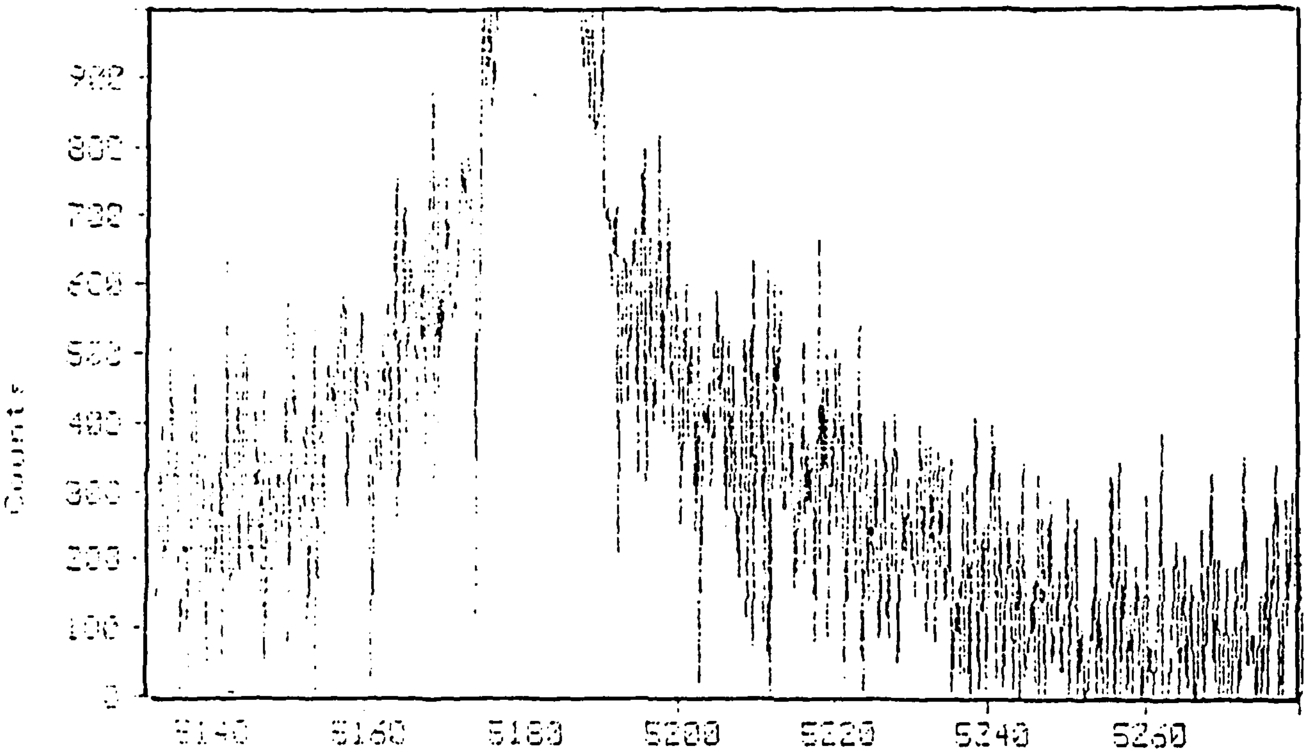


Figure 18. Induced Fluorescence (Laser at 5181.5 Å), 5130-5280 Å

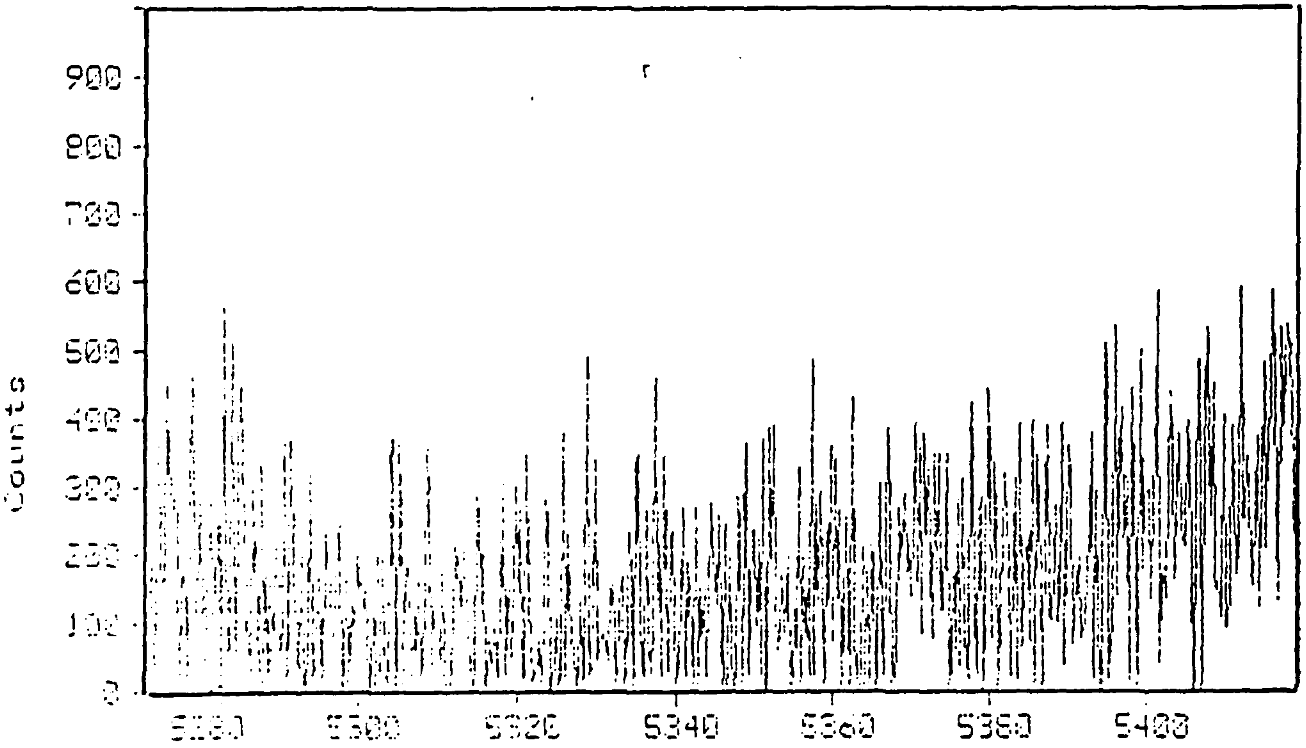


Figure 19. Induced Fluorescence (Laser at 5181.5 Å), 5270-5420 Å

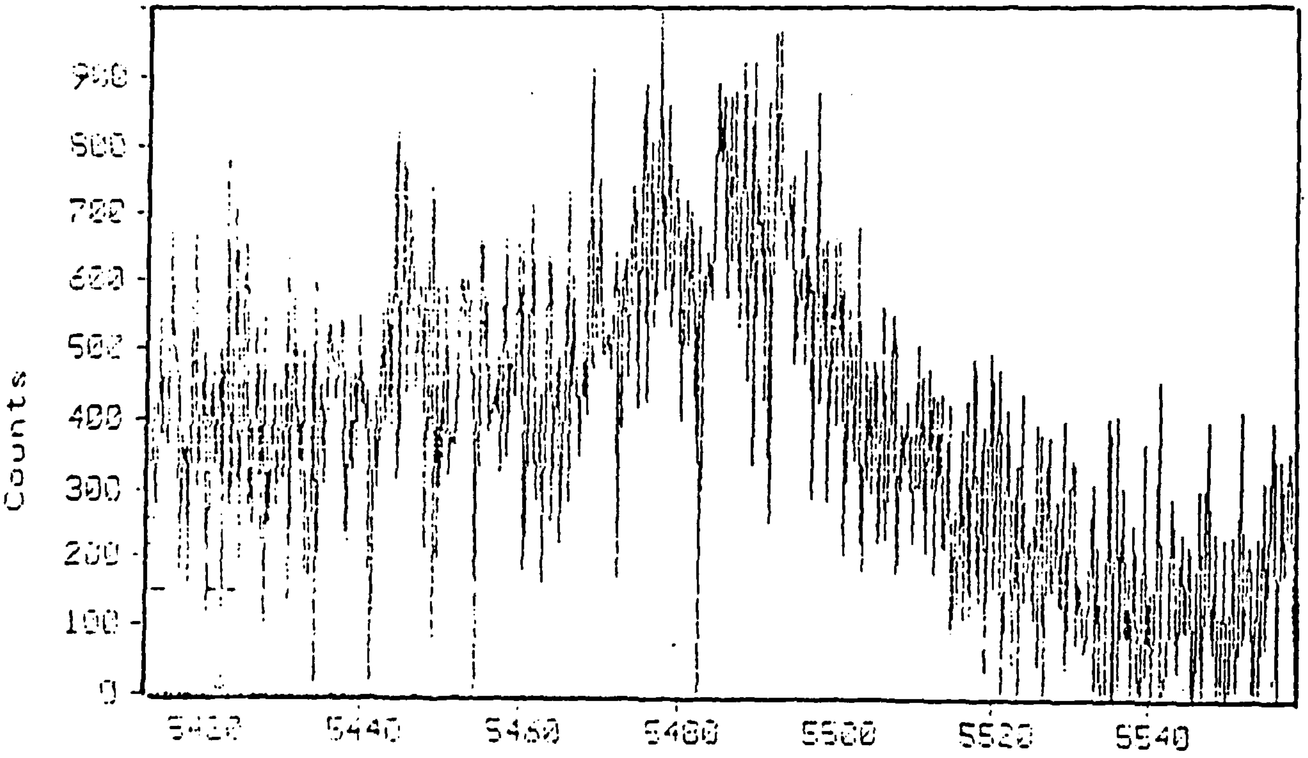


Figure 20. Induced Fluorescence (Laser at 5181.5 Å), 5410-5560 Å

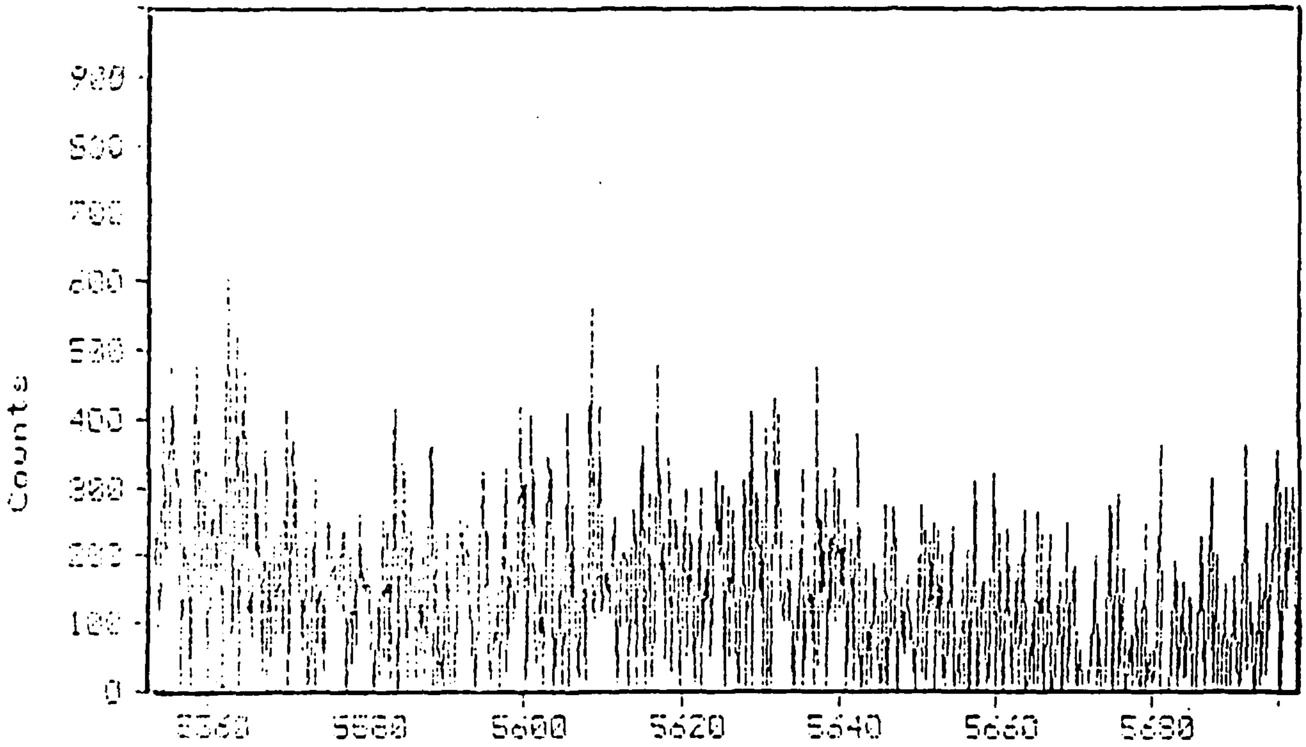


Figure 21. Induced Fluorescence (Laser at 5181.5 Å), 5550-5700 Å

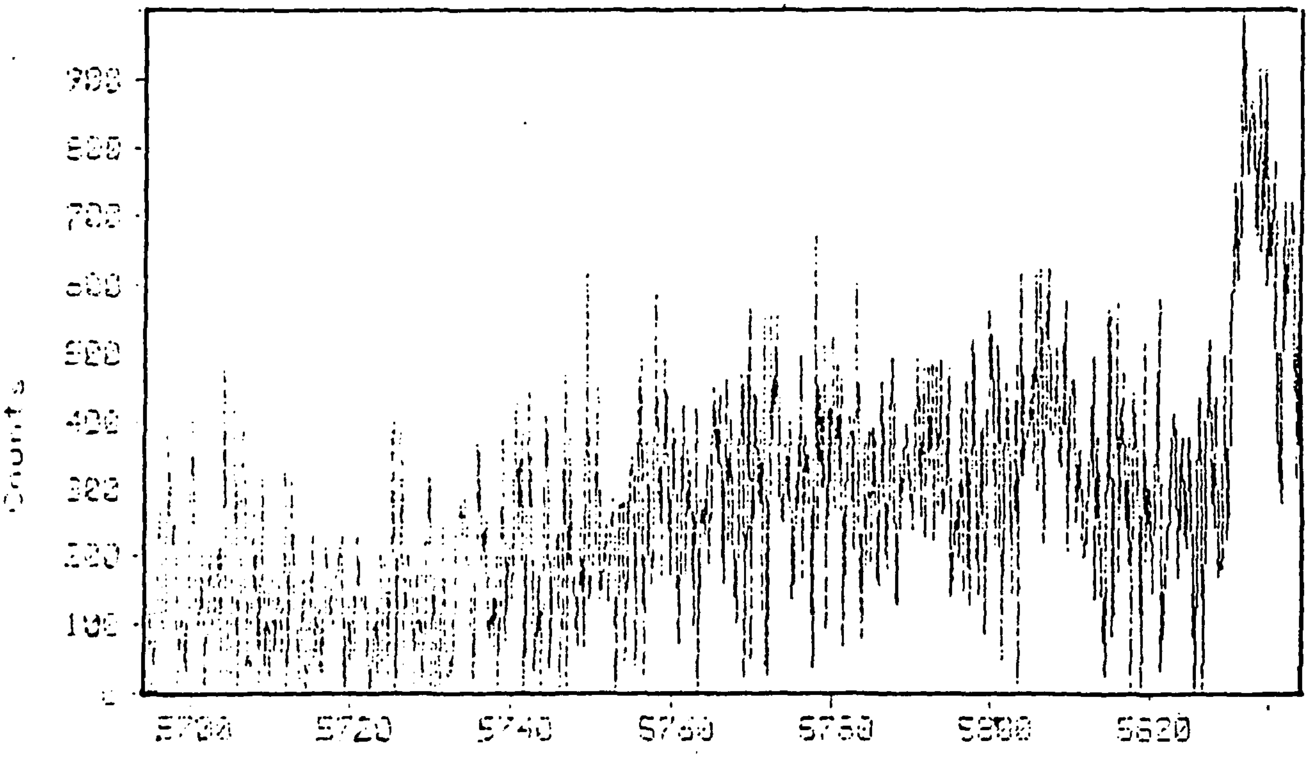


Figure 22. Induced Fluorescence (Laser at 5181.5 Å), 5690-5840 Å

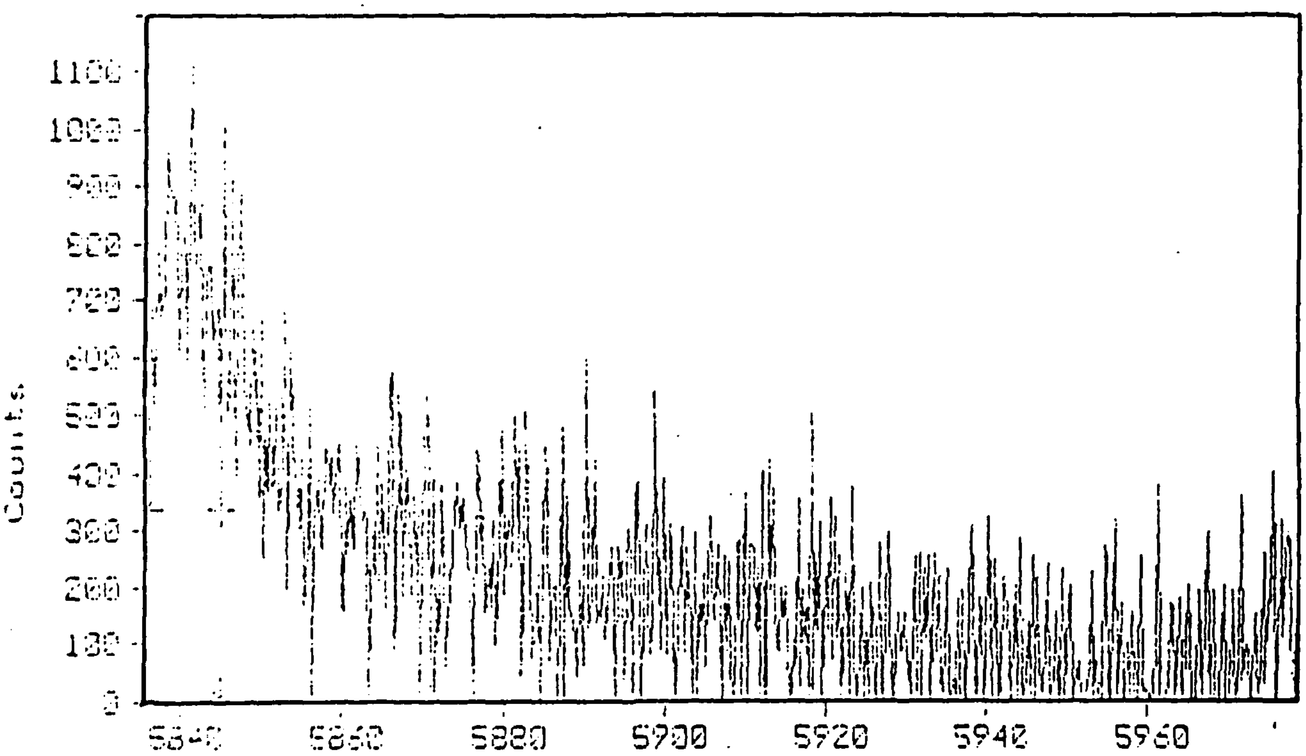


Figure 23. Induced Fluorescence (Laser at 5181.5 Å), 5830-5980 Å

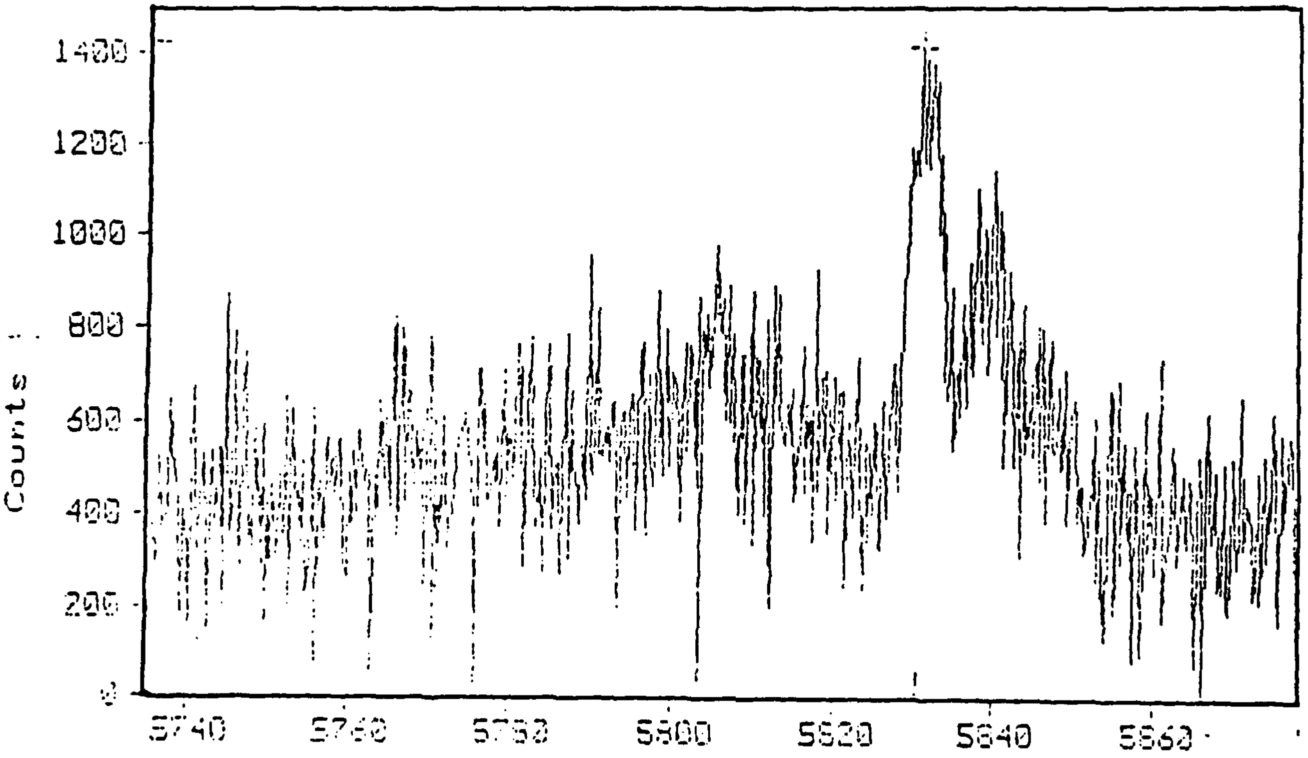


Figure 24. Induced Fluorescence (Laser at 5181.5 Å), 5730-5880 Å

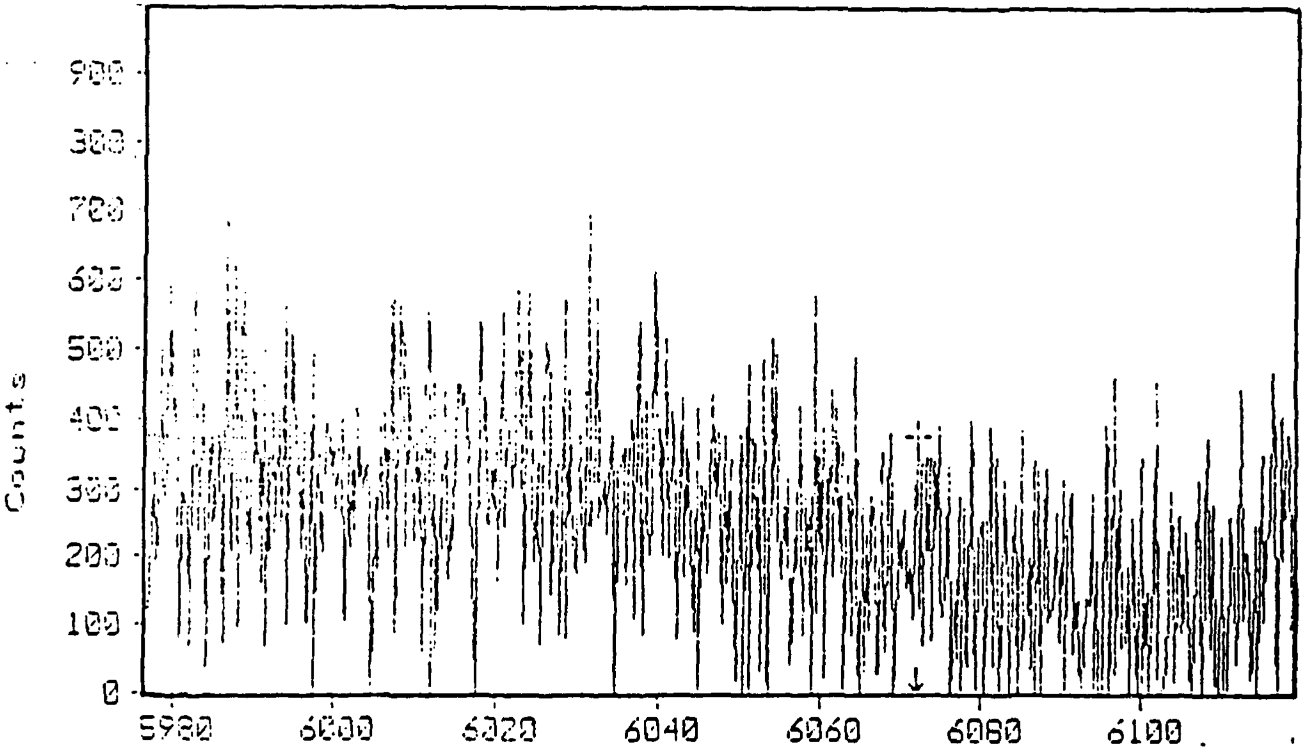


Figure 25. Induced Fluorescence (Laser at 5181.5 Å), 5970-6120 Å

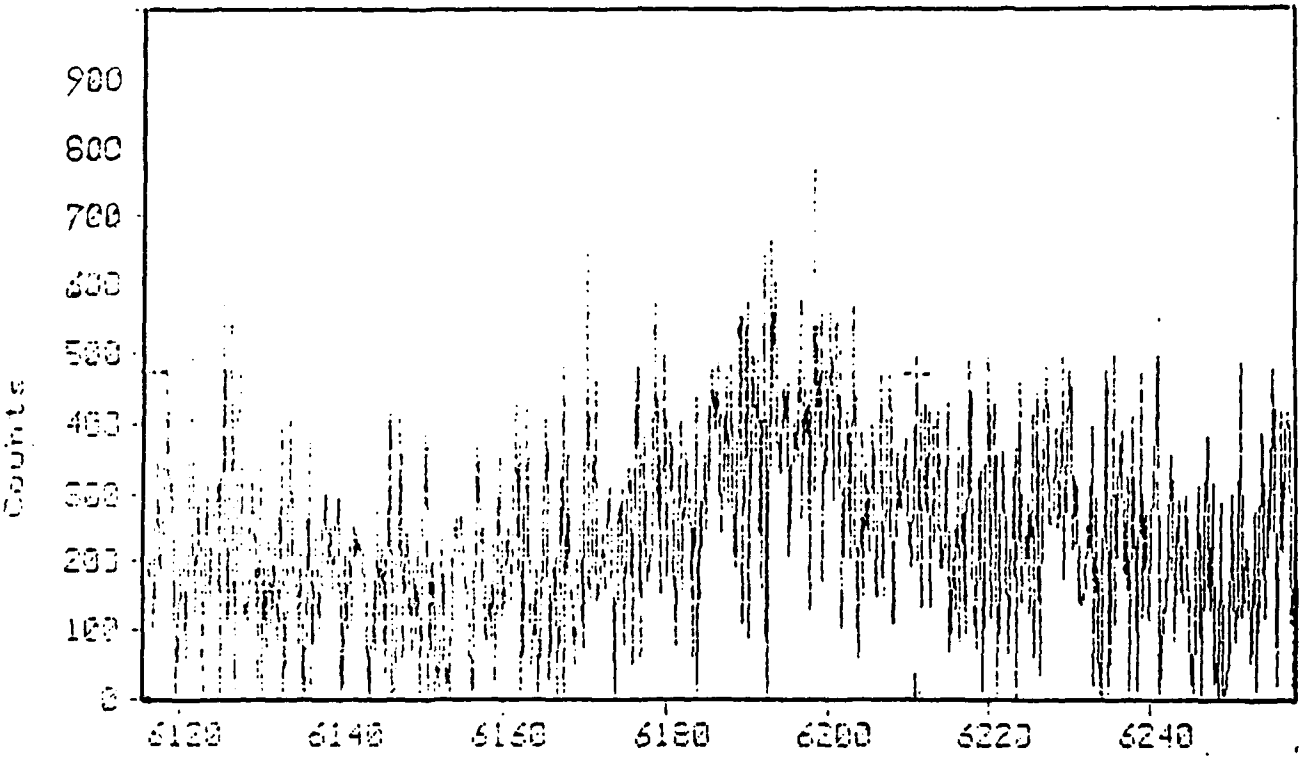


Figure 26. Induced Fluorescence (Laser at 5181.5 Å), 6110-6260 Å

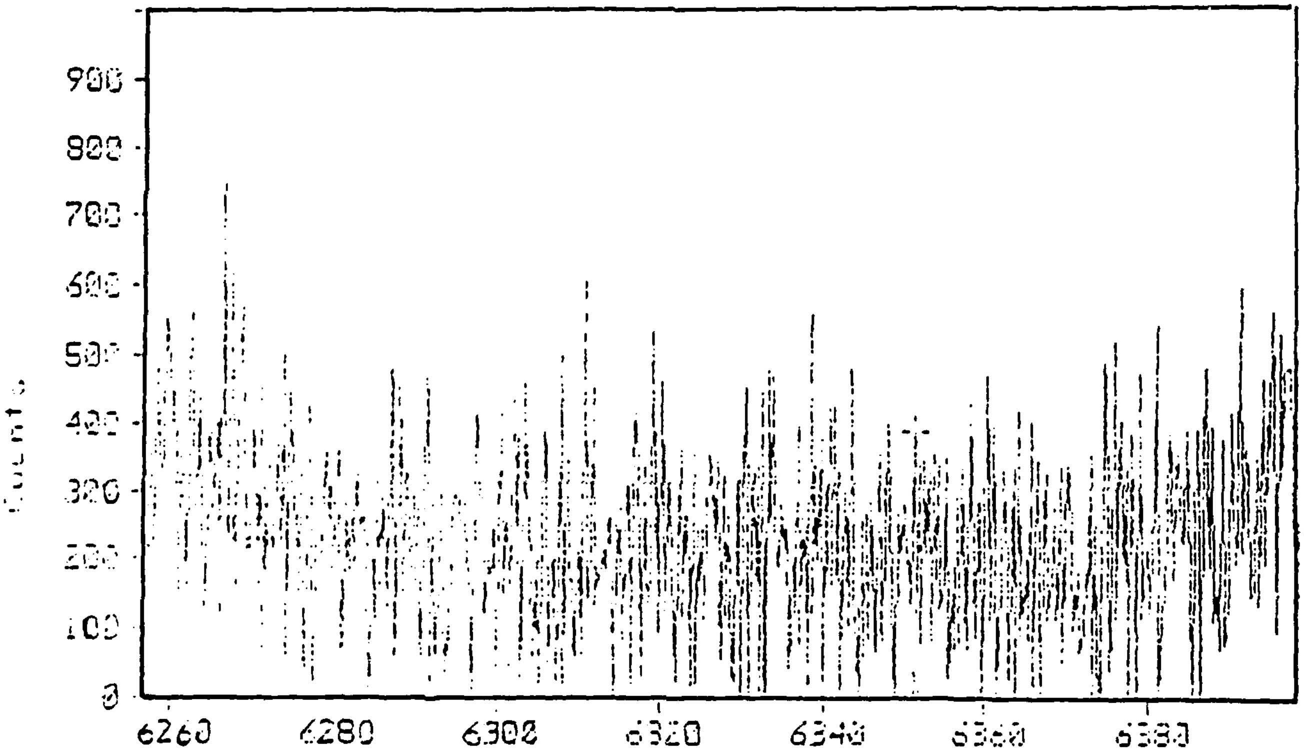


Figure 27. Induced Fluorescence (Laser at 5181.5 Å), 6250-6400 Å

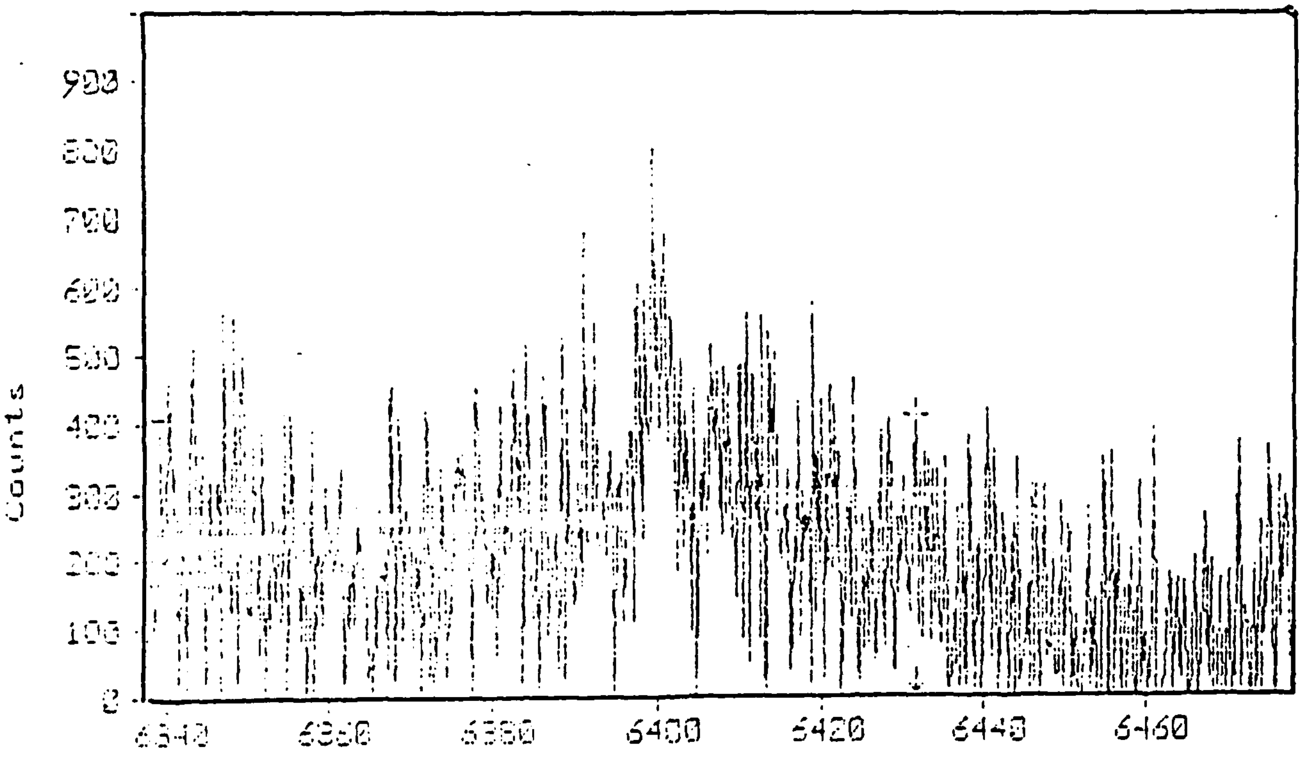


Figure 28. Induced Fluorescence (Laser at 5181.5 Å), 6330-6480 Å

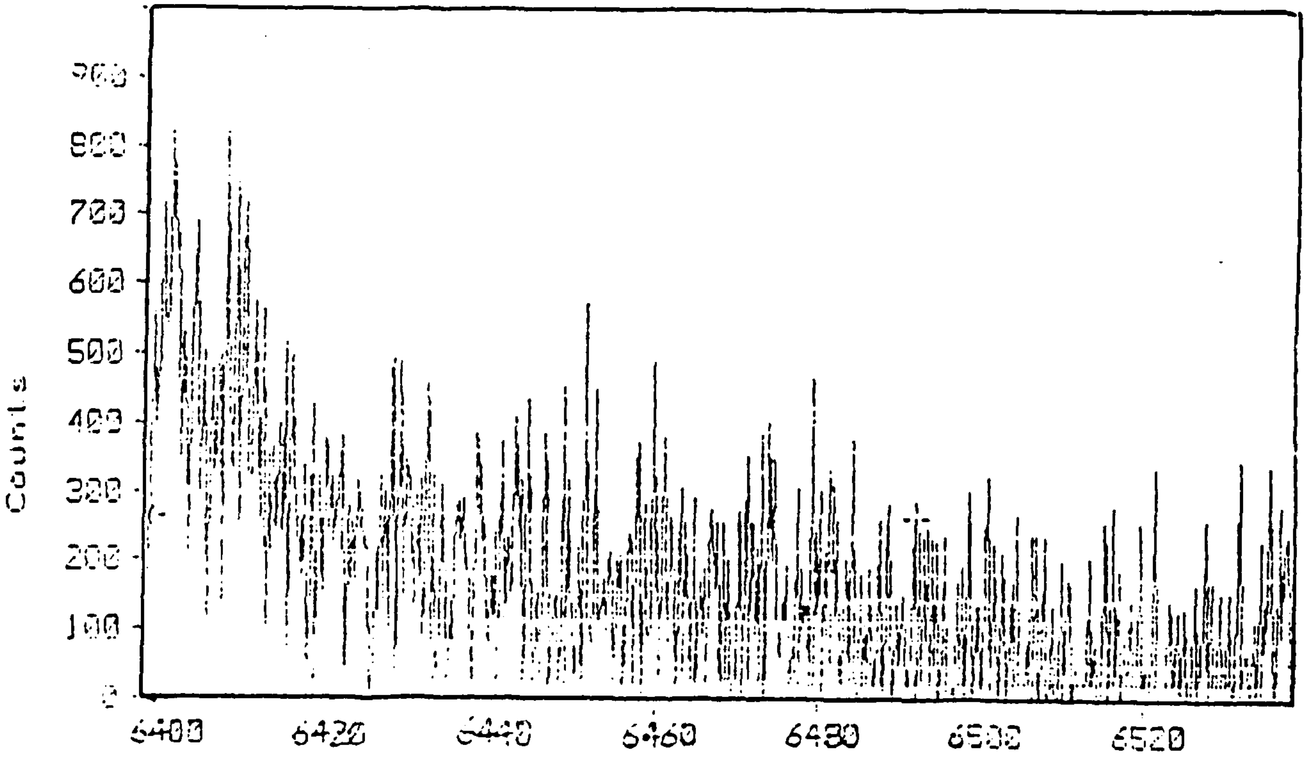


Figure 29. Induced Fluorescence (Laser at 5181.5 Å), 6400-6540 Å

Appendix B: Laser-Induced Fluorescence Survey Spectra

The following figures illustrate the laser-induced fluorescence produced with exciting the R1 band of the (00^00-00^00) transition of BO_2 in the atmospheric pressure flame:

Mix: CH_4/Dry Air/O_2/BCl_3

Pump: 5471 Å, 13 mJ per pulse

Spectrometer Slits: 200 microns

Scans: 200

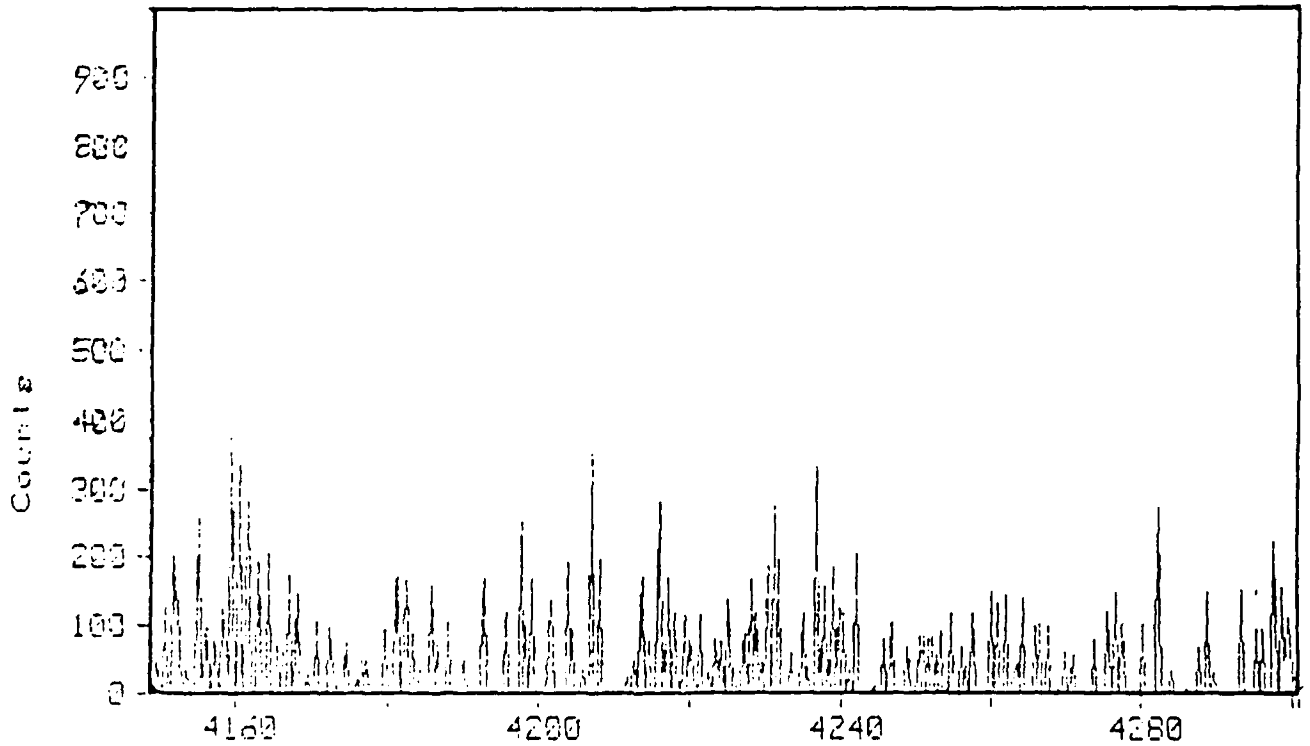


Figure 30. Induced Fluorescence (Laser at 5471 Å), 4150-4300 Å

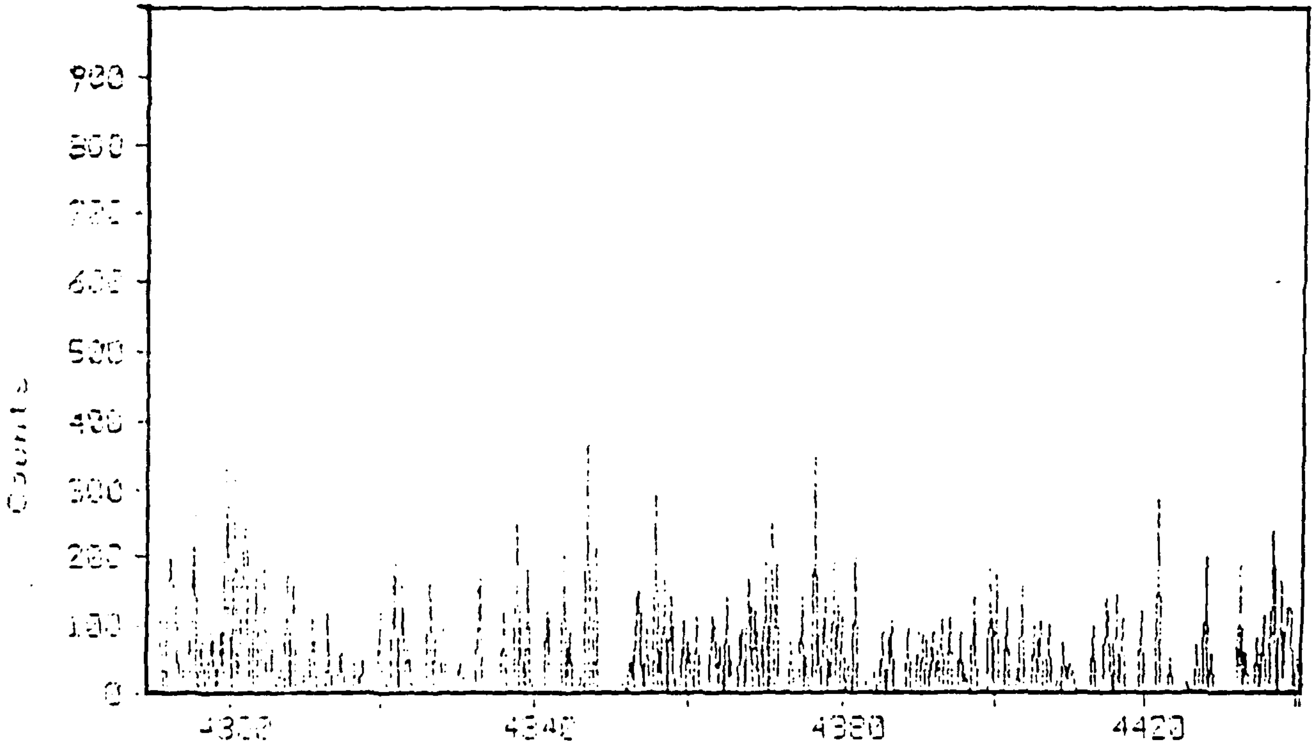


Figure 31. Induced Fluorescence (Laser at 5471 Å), 4290-4440 Å

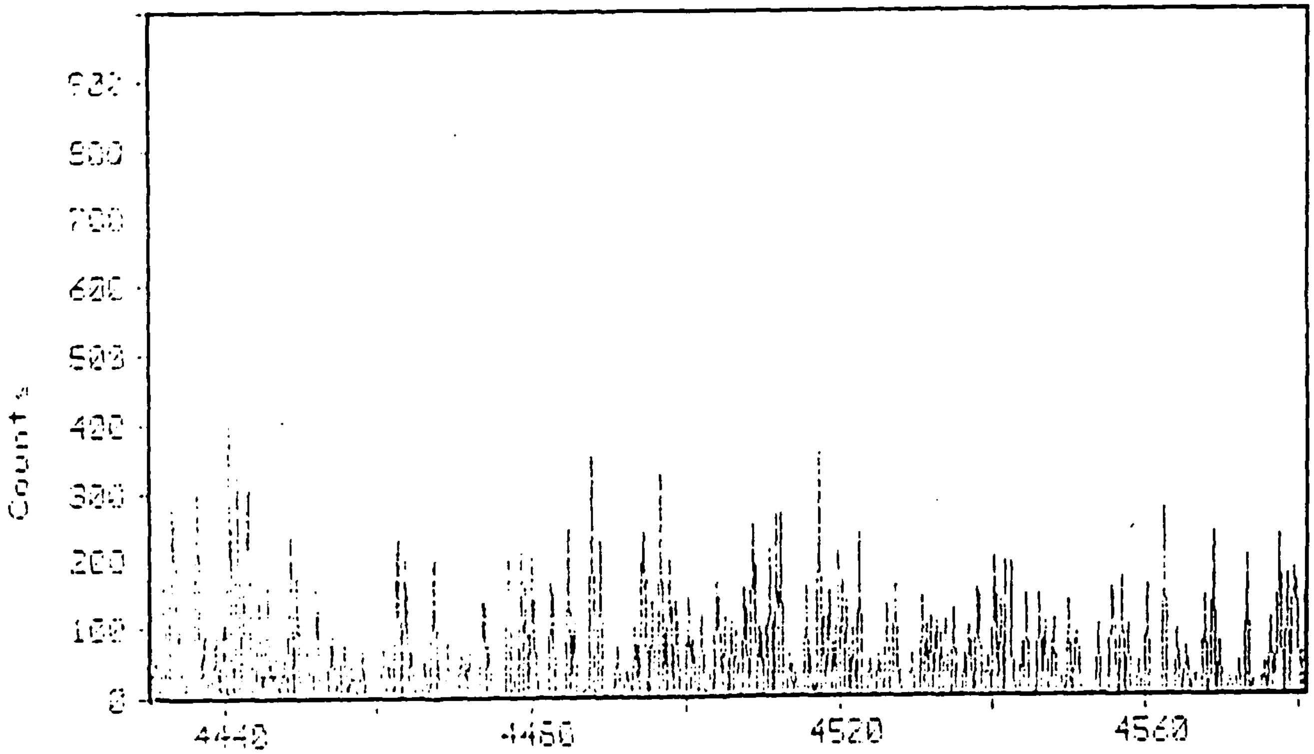


Figure 32. Induced Fluorescence (Laser at 5471 Å), 4430-4580 Å

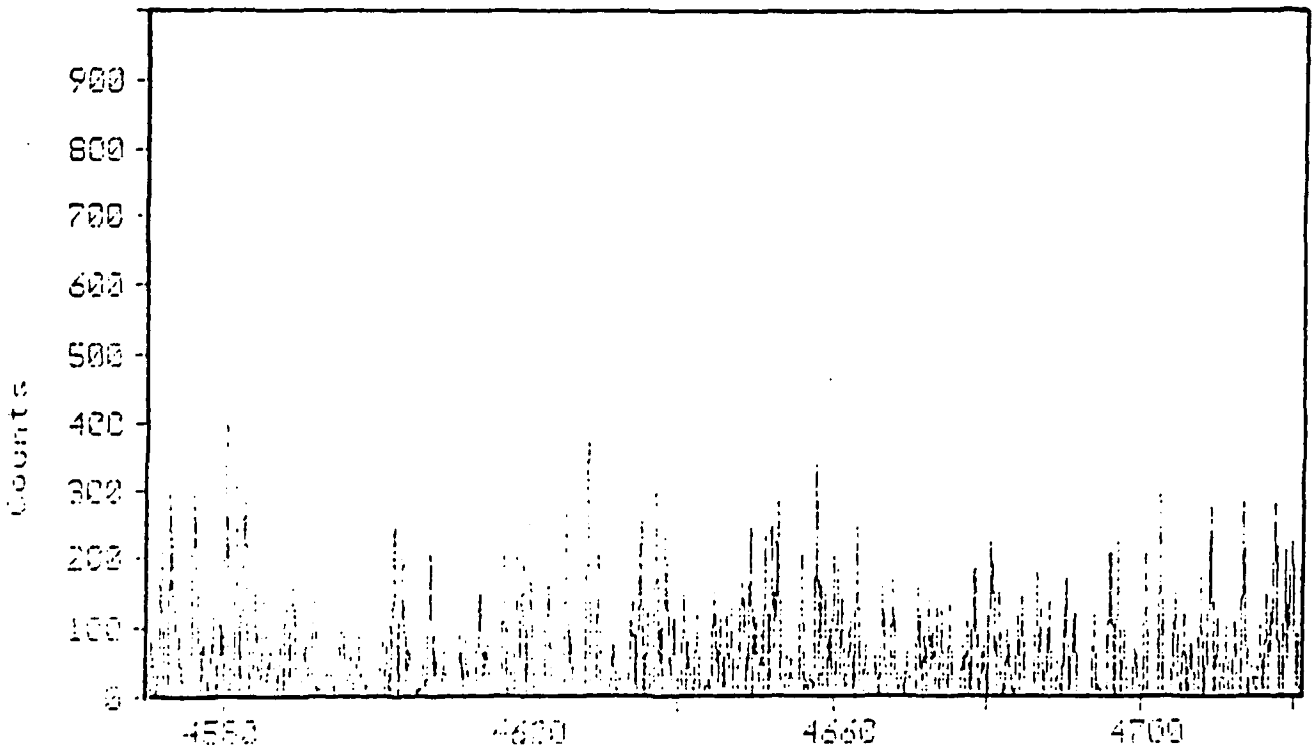


Figure 33. Induced Fluorescence (Laser at 5471 Å), 4570-4720 Å

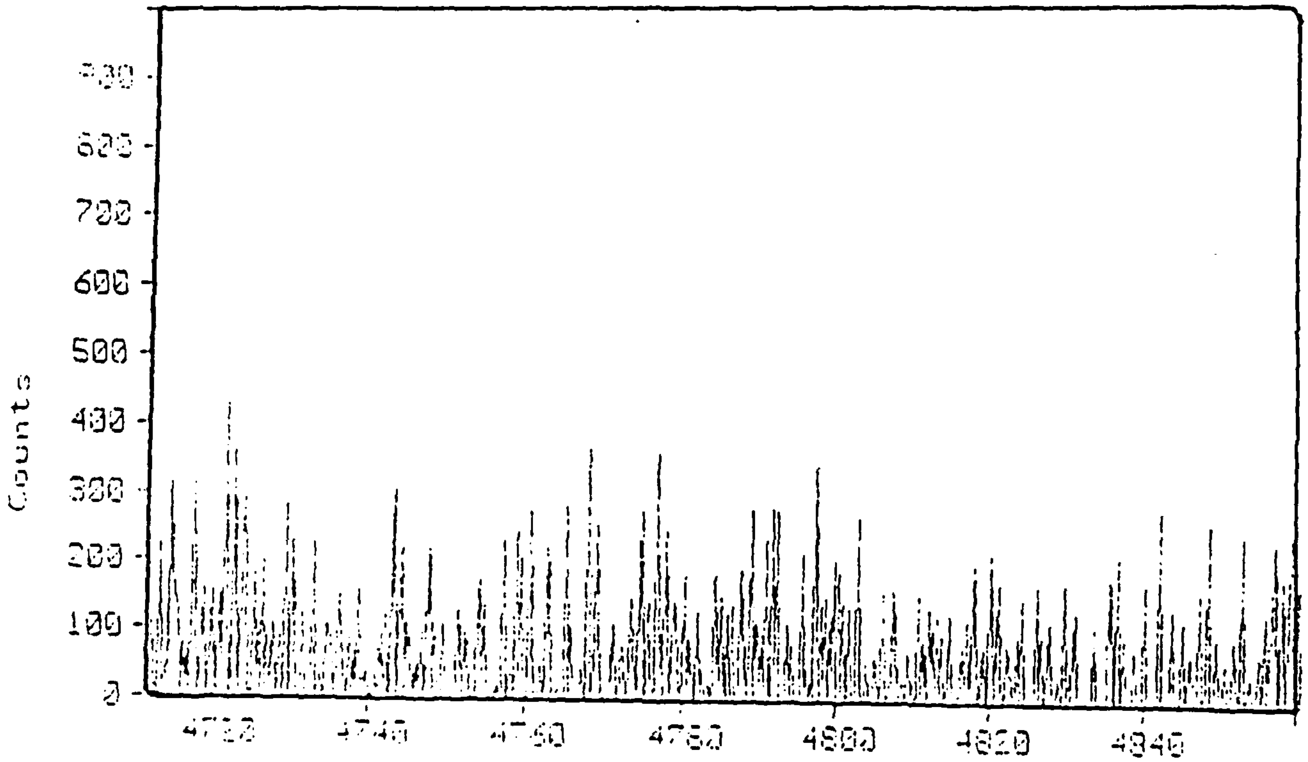


Figure 34. Induced Fluorescence (Laser at 5471 Å), 4710-4860 Å

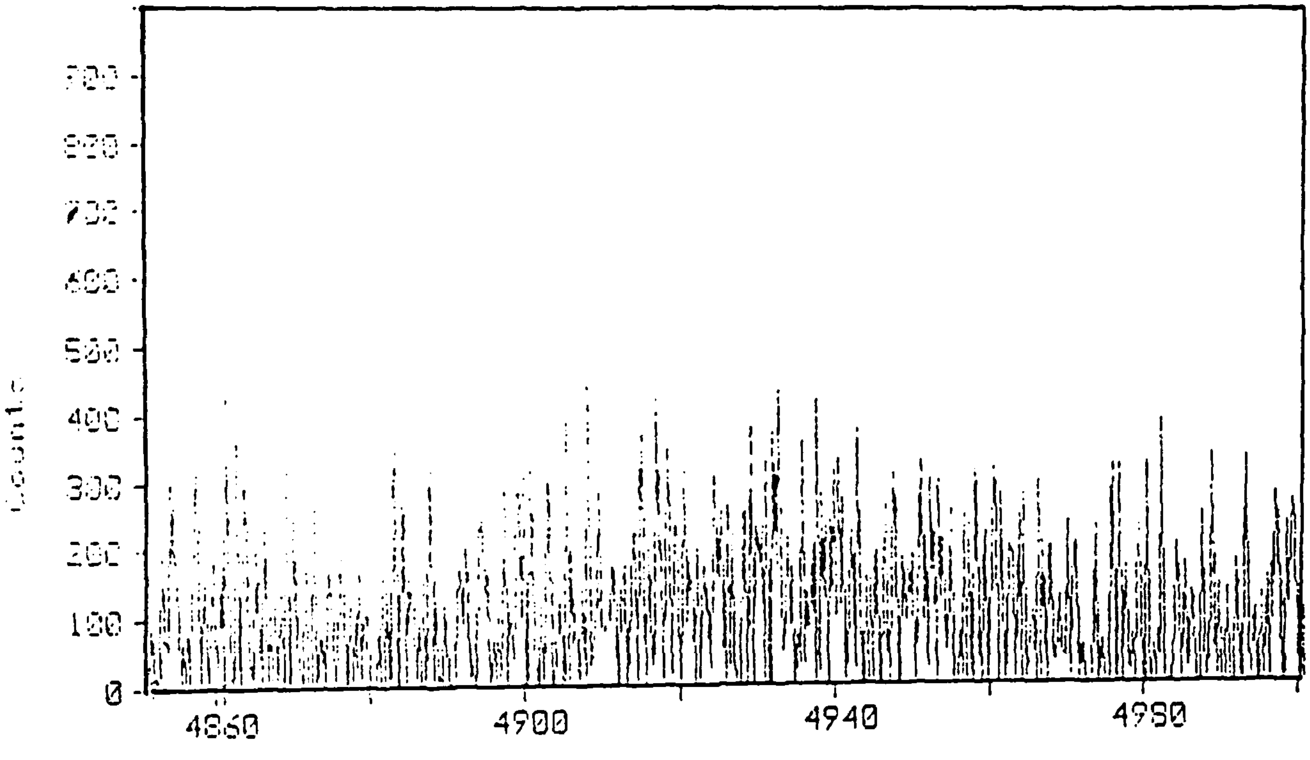


Figure 35. Induced Fluorescence (Laser at 5471 Å), 4850-5000 Å

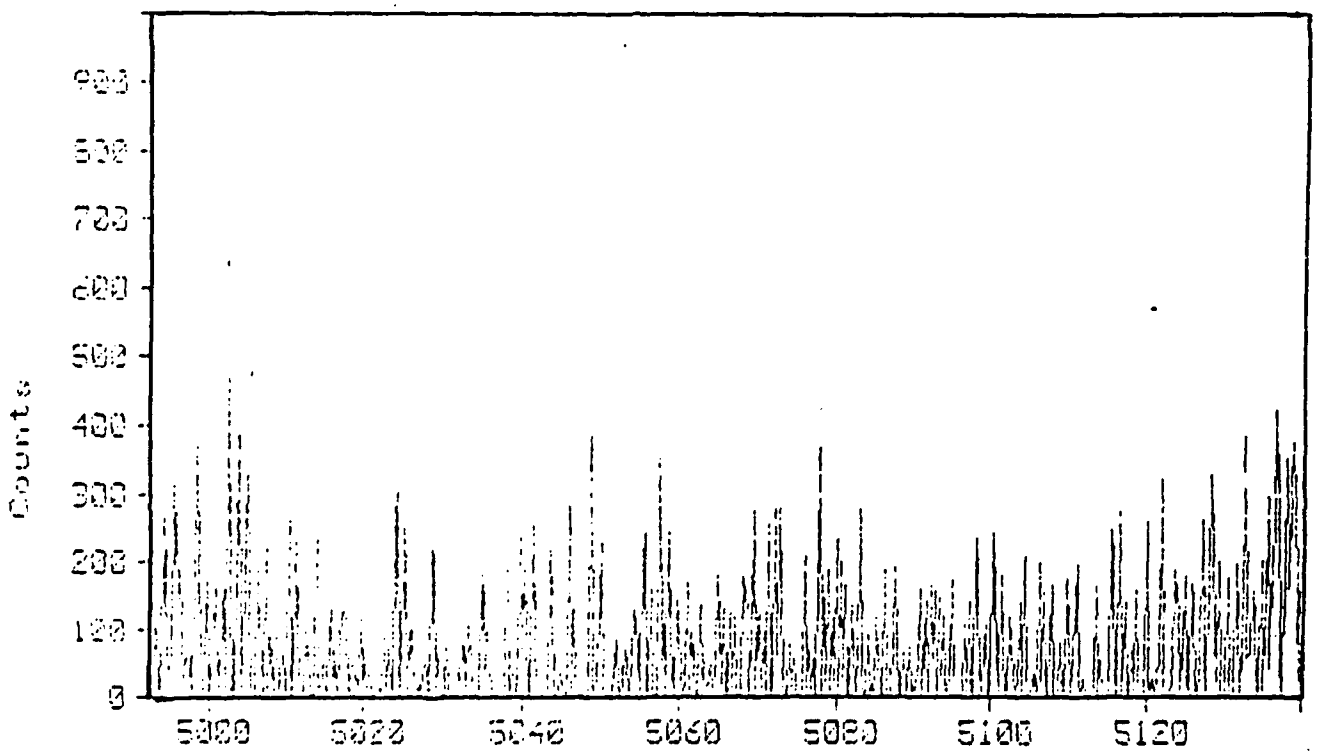


Figure 36. Induced Fluorescence (Laser at 5471 Å), 4990-5140 Å

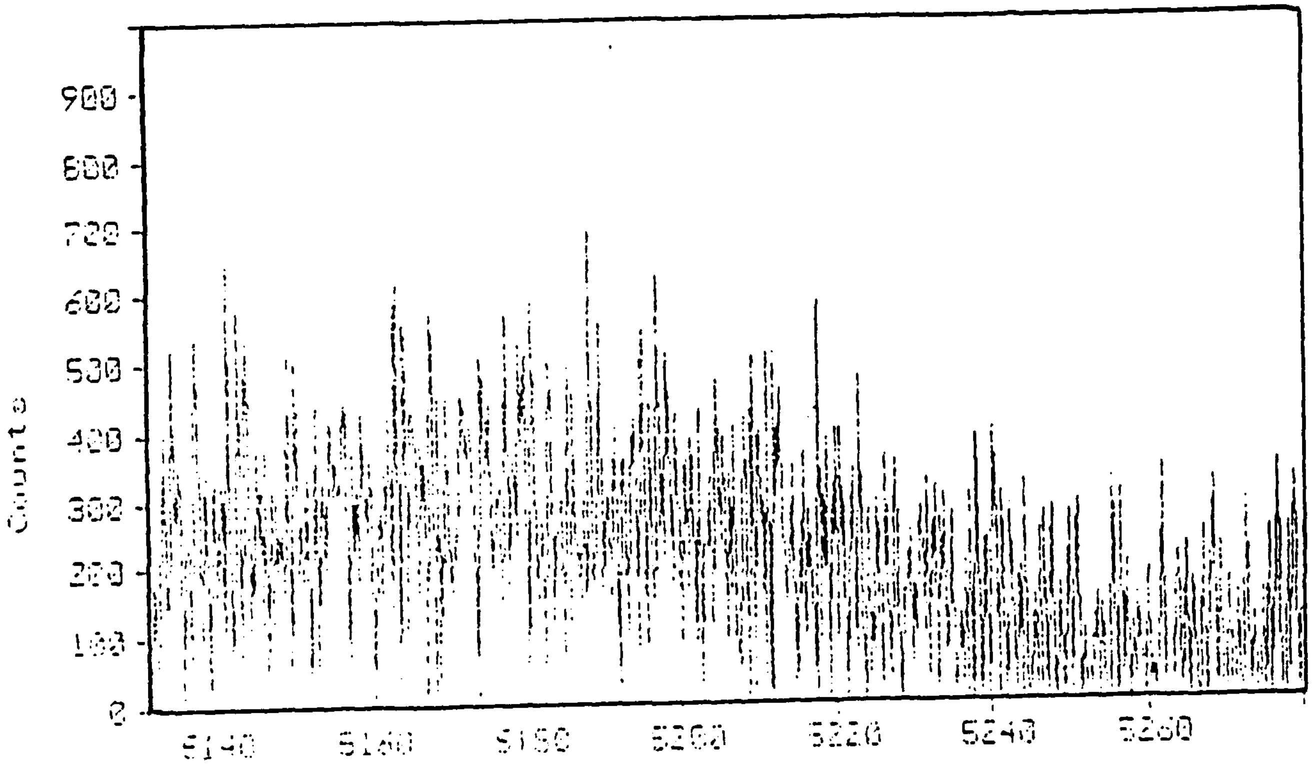


Figure 37. Induced Fluorescence (Laser at 5471 Å), 5130-5280 Å

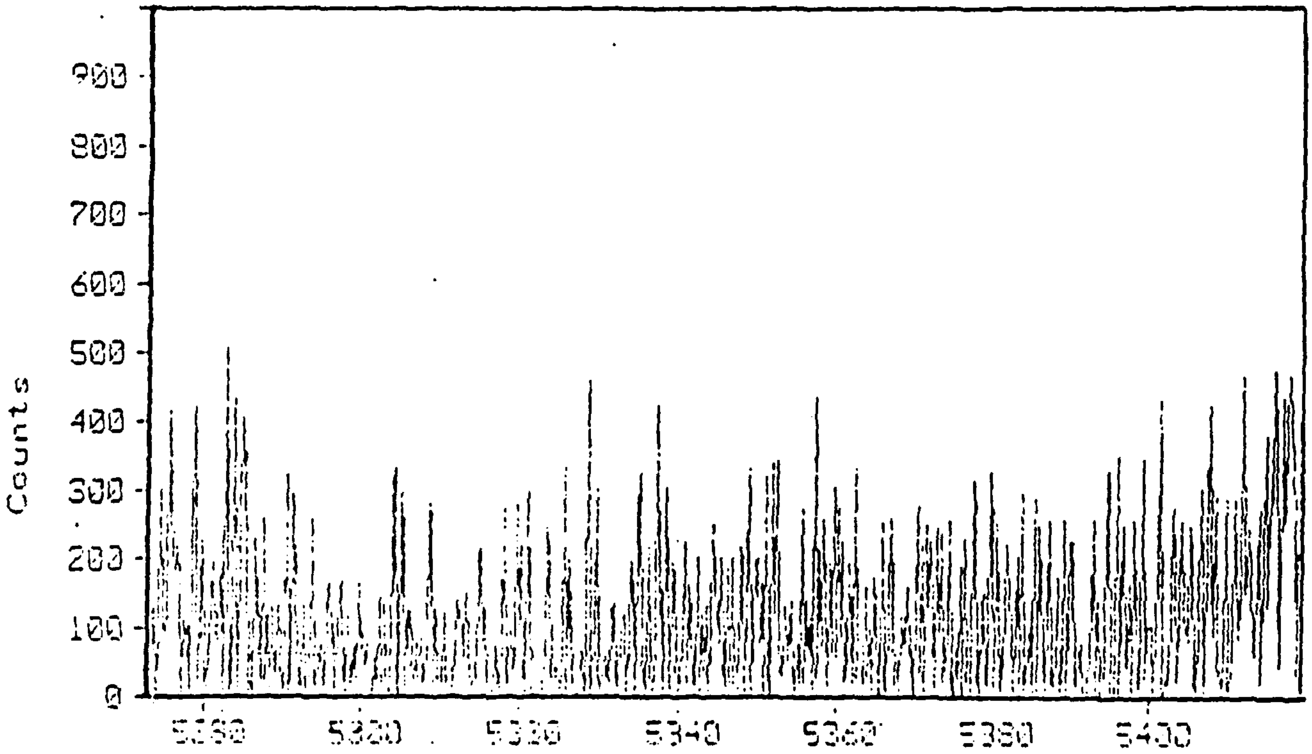


Figure 38. Induced Fluorescence (Laser at 5471 Å), 5270-5420 Å

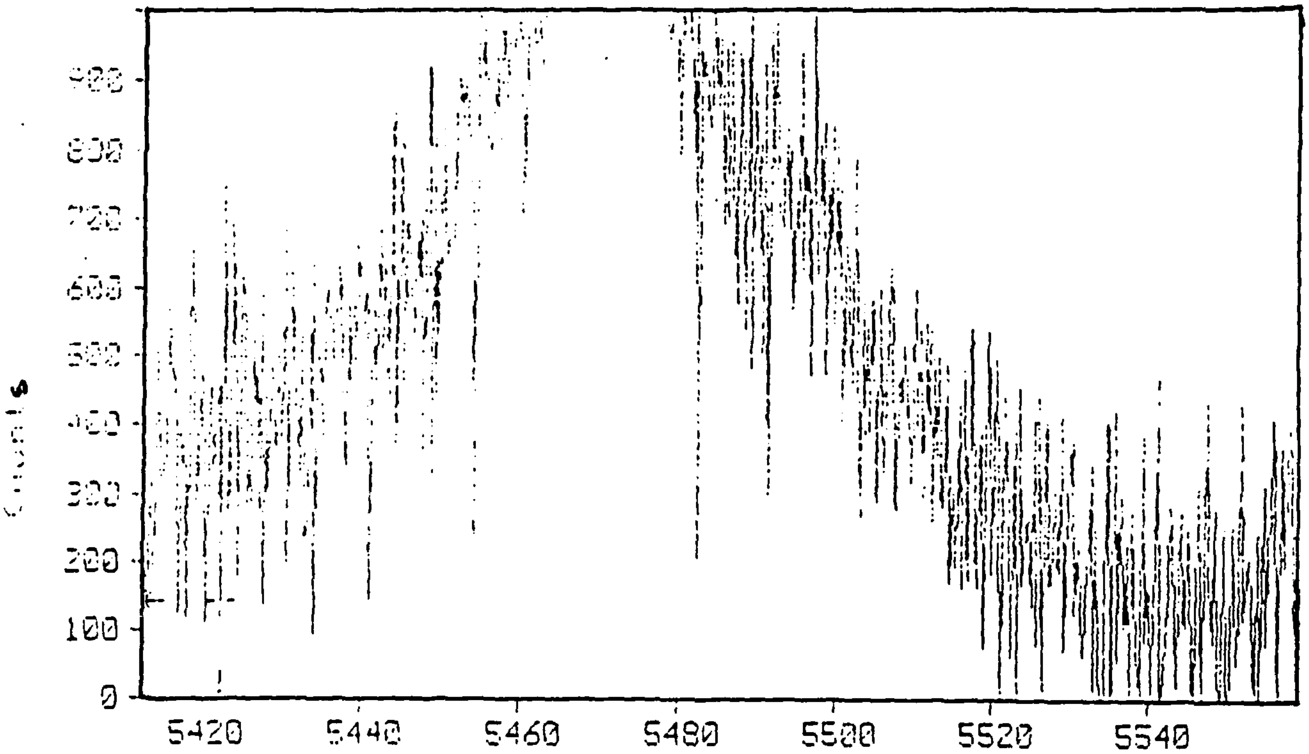


Figure 39. Induced Fluorescence (Laser at 5471 Å), 5410-5560 Å

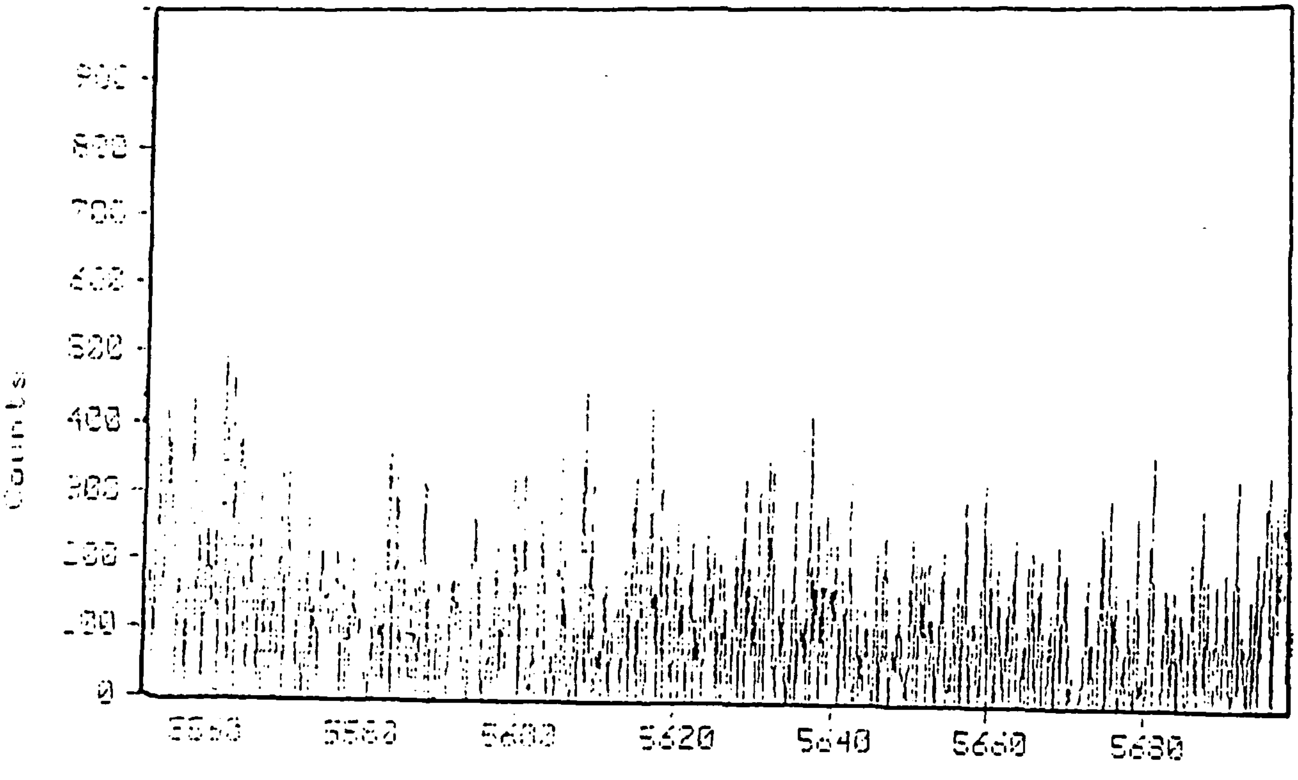


Figure 40. Induced Fluorescence (Laser at 5471 Å), 5550-5700 Å

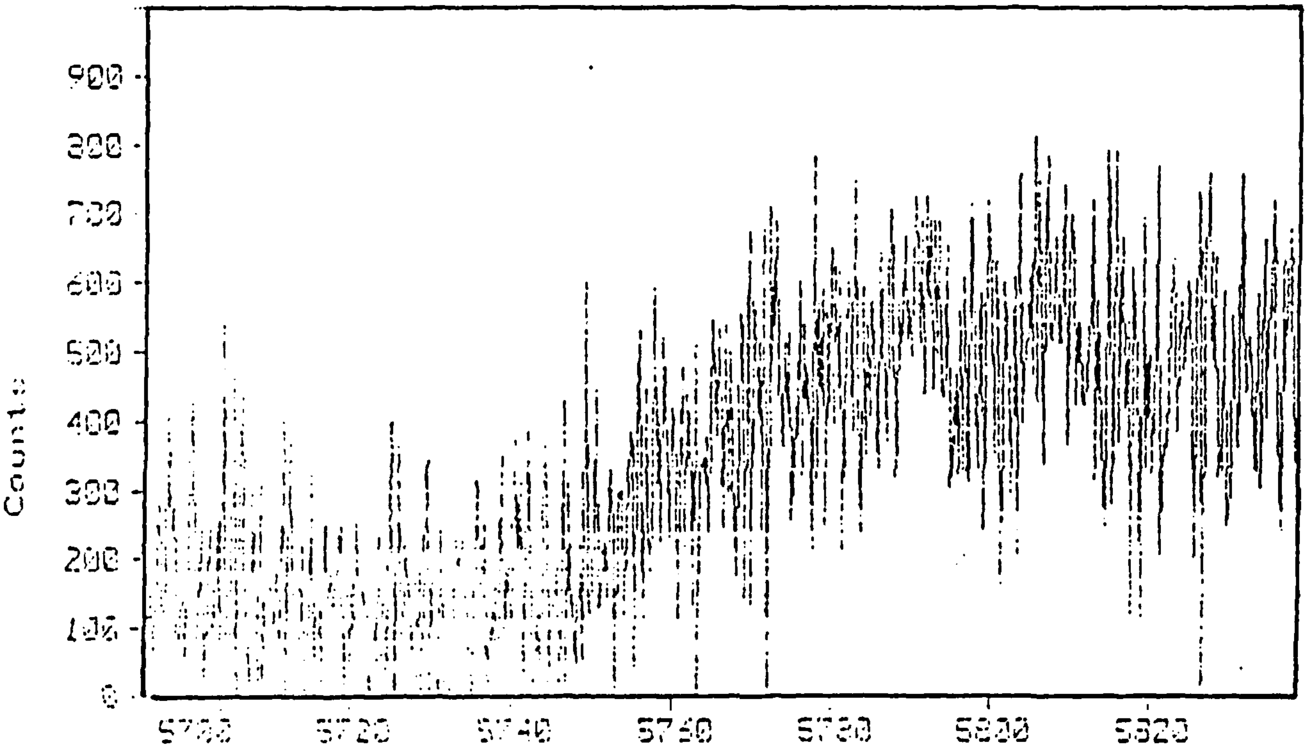


Figure 41. Induced Fluorescence (Laser at 5471 Å), 5690-5840 Å

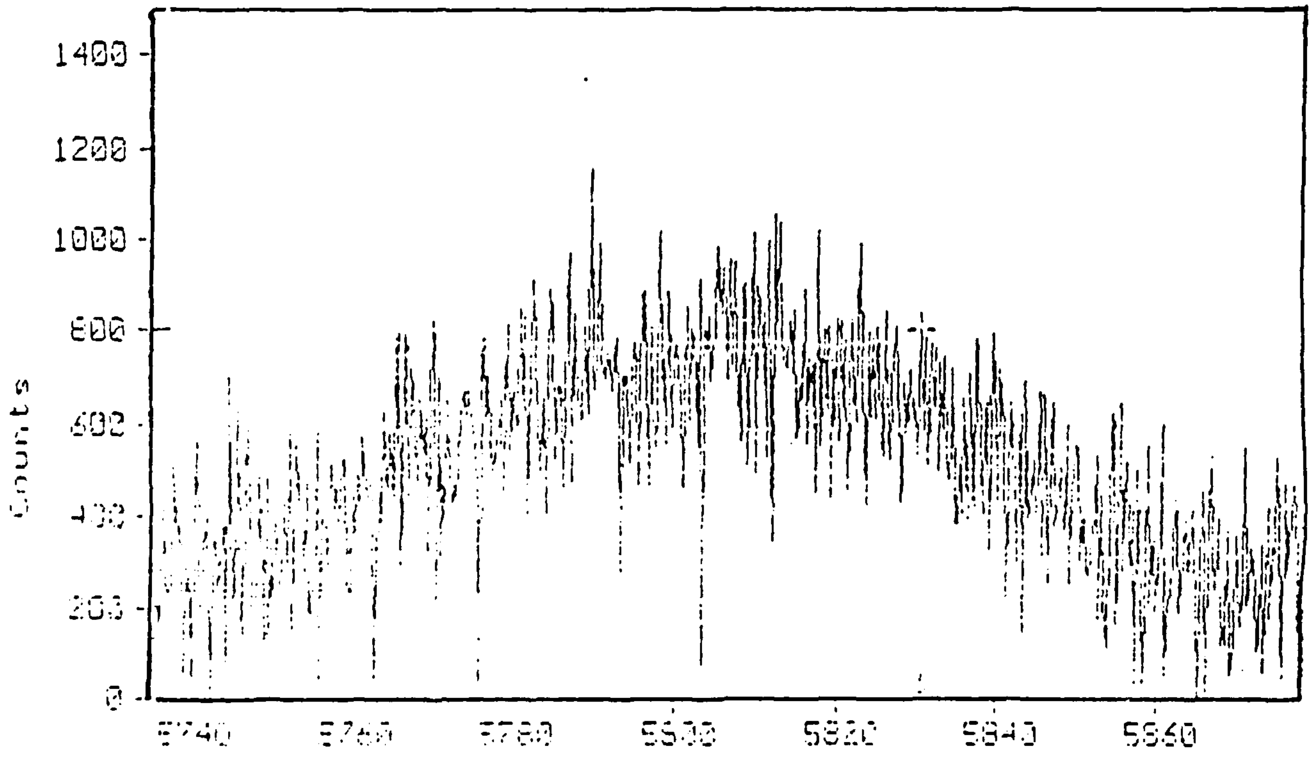


Figure 42. Induced Fluorescence (Laser at 5471 Å), 5730-5880 Å

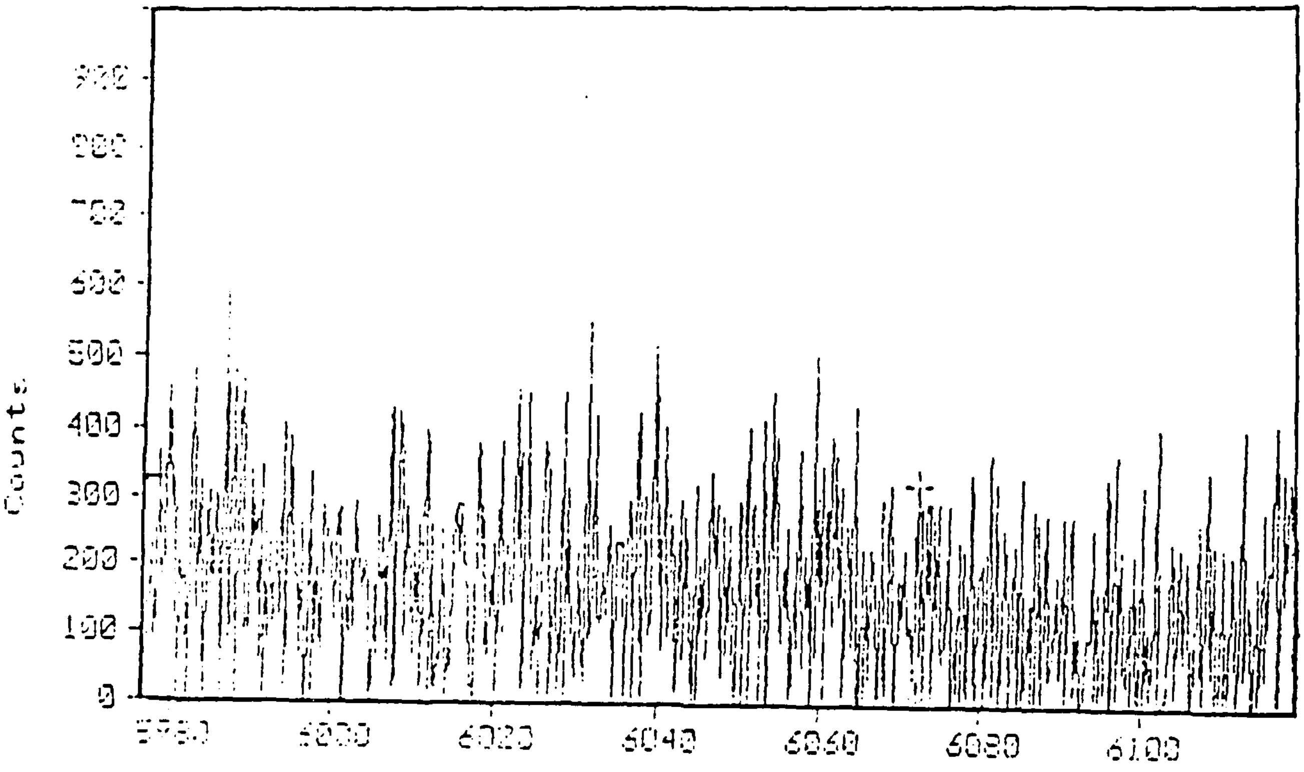


Figure 43. Induced Fluorescence (Laser at 5471 Å), 5970-6120 Å

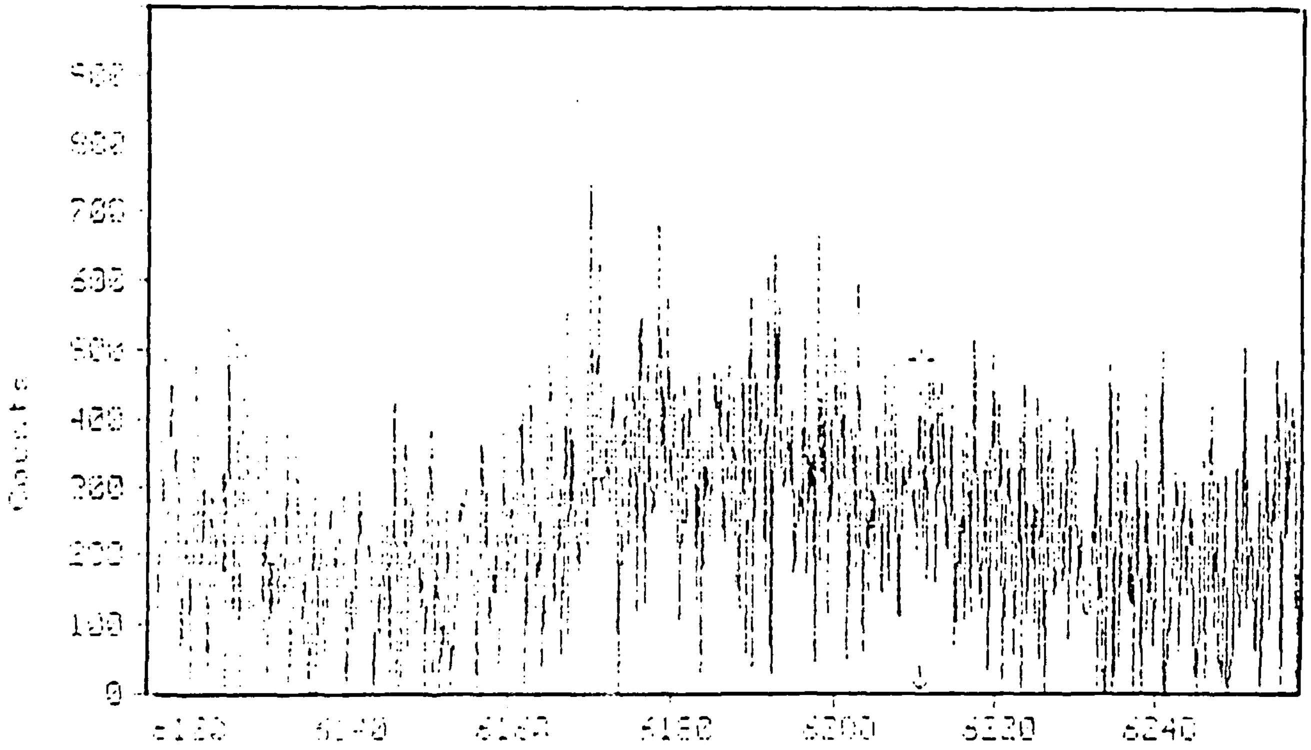


Figure 44. Induced Fluorescence (Laser at 5471 Å), 6110-6260 Å

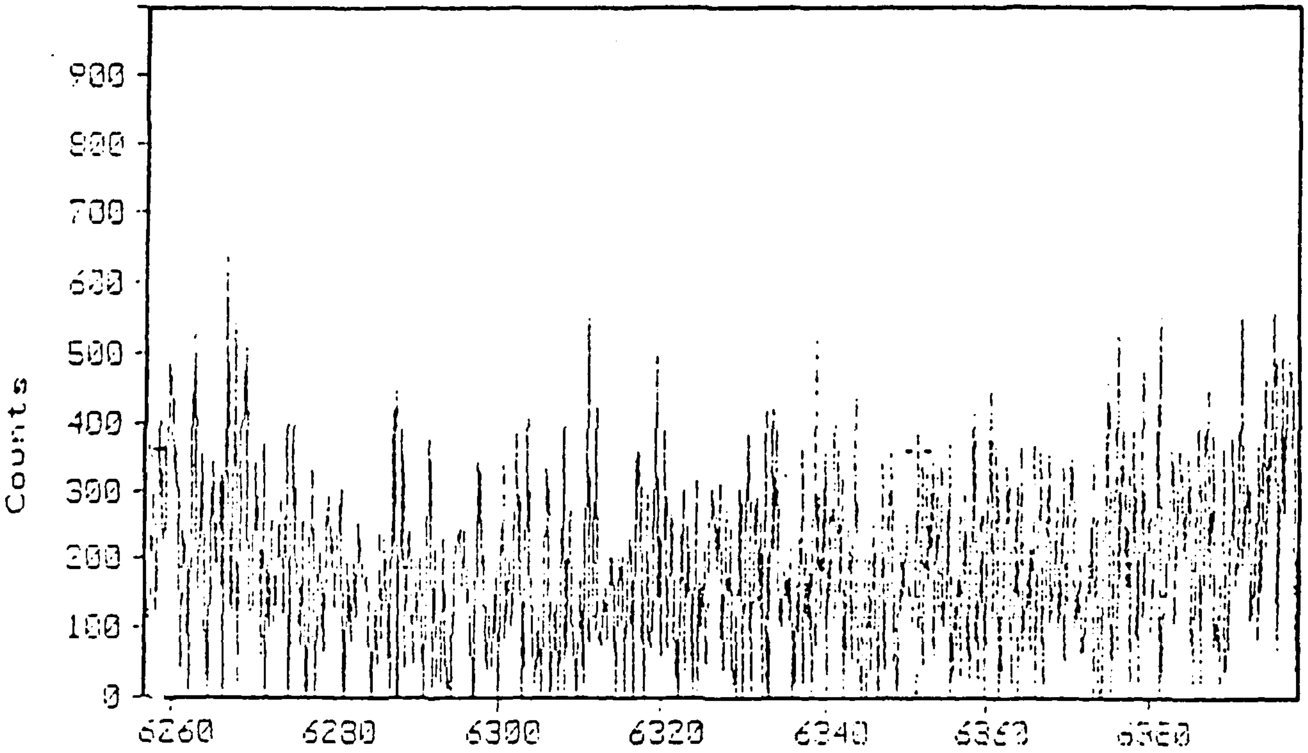


Figure 45. Induced Fluorescence (Laser at 5471 Å), 6250-6400 Å

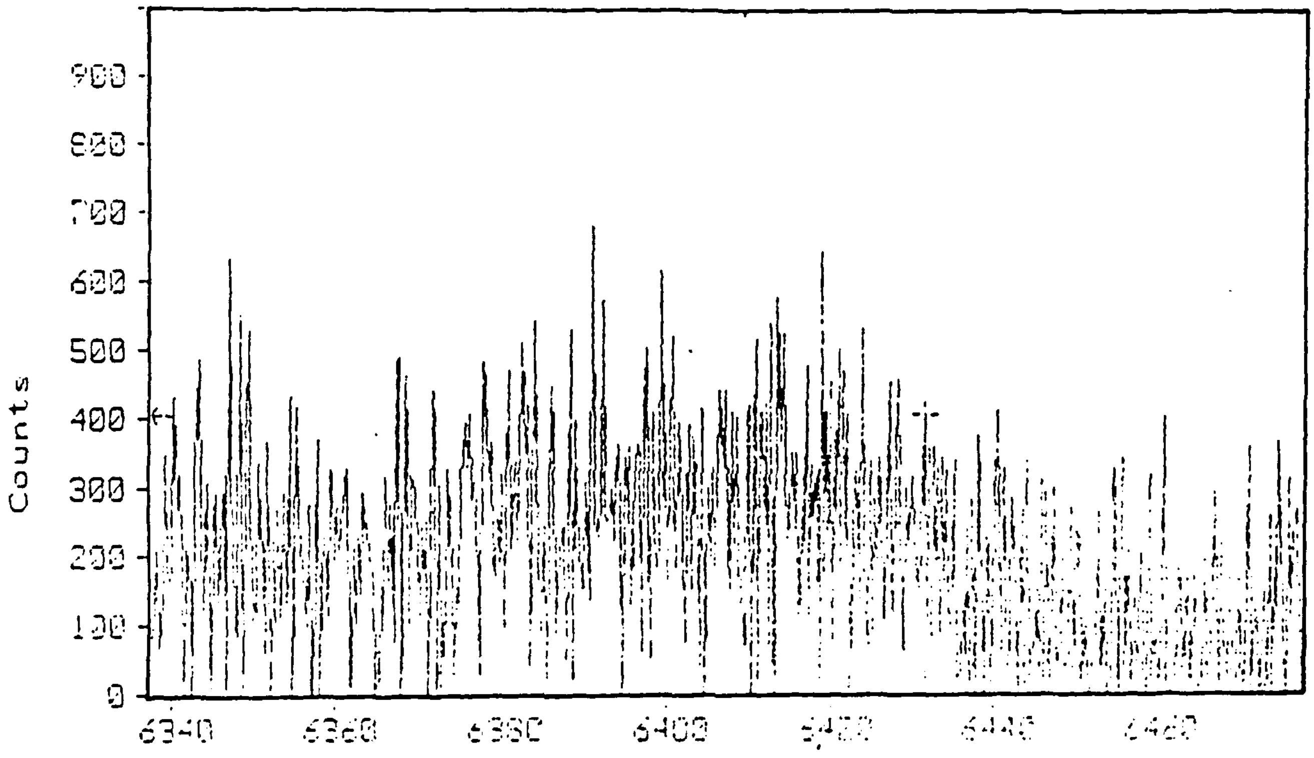


Figure 46. Induced Fluorescence (Laser at 5471 Å), 6330-6480 Å

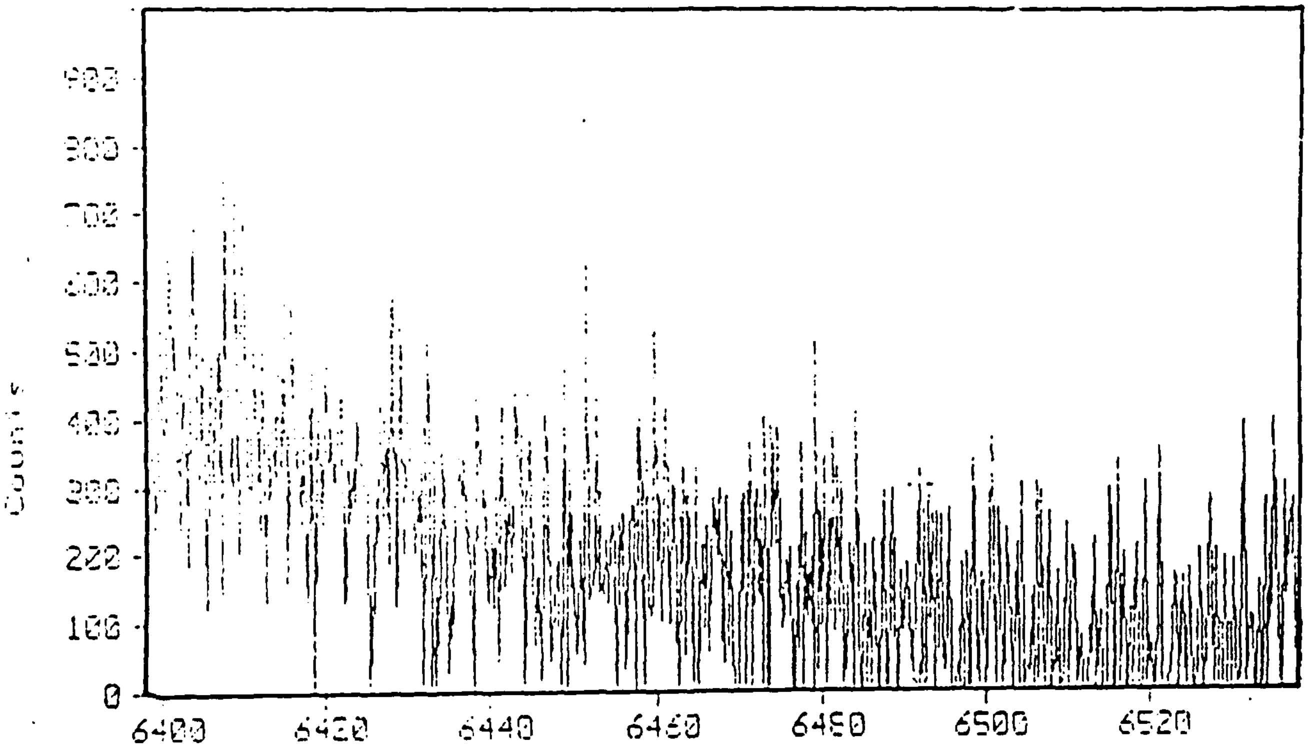


Figure 47. Induced Fluorescence (Laser at 5471 Å), 6400-6540 Å

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Vita

Major Jong W. Cha [redacted] He graduated from high school in Yeosu in 1977 and attended the Korean Air Force Academy, from which he received a Bachelor of Science degree in Electrical Engineering and a regular commission in the Korean Air Force in 1981. He completed pilot training and received his wings in 1981. He then served as a F-5E pilot and flight instructor until entering the School of Engineering, Air Force Institute of Technology, in June 1987.

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The puopose of this project was to demonstrate the feasibility of a laser-induced fluorescence (LIF) technique for determining the concentration of boron compounds in an atmospheric-pressure, boron seeded flame. Such a demonstration would provide a useful tool to investigate the detailed combustion chemistry of boron fuels. The two radical species which are thought to be the most important reaction intermediates in the boron combustion process, BO and BO_2, were sought.

A burner was used to produce a ~~CH_4/dry~~ air/O_2 flame, then BCl_3 was added to the flame. This burner was movable in two directions, so various regions of the flame could be investigated easily.

A tunable pulsed dye laser which was pumped by an excimer laser was used to match the absorption bands of BO and BO_2. Good LIF signals of BO_2 were readily achieved, then the optimum band for LIF diagnostics of BO_2 was sought. The excitation of the (10°0-00°0) band followed by fluorescence detection of the (10°0-20°0) band was the optimum choice. Although a rather extensive search for LIF signal of BO was conducted, no LIF signal attributable to BO was detected. The most possible reason for this negative result was thought to be a heavy quenching under a high-pressure environment. [illegible] lasers; [illegible] boron; laser induced fluorescence; (KT)