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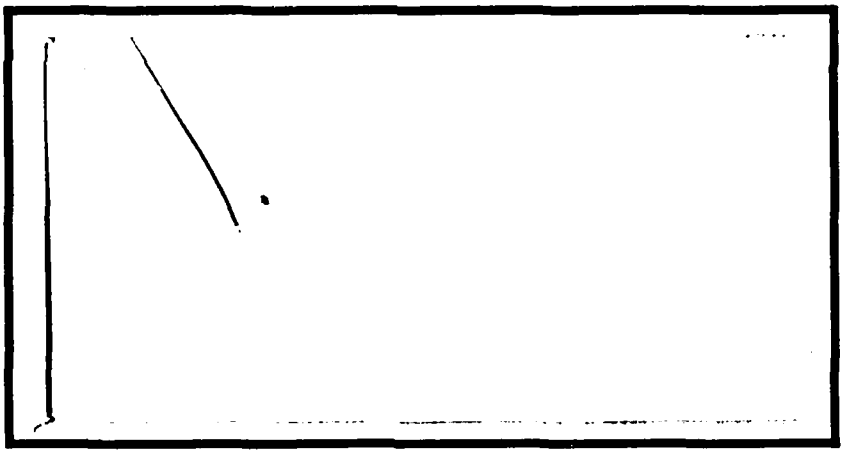

DEPARTMENT OF THE AIR FORCE

AIR UNIVERSITY

AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

AFIT/GE/ENP/88D-3

COLLISIONAL ENERGY TRANSFER MECHANISMS BETWEEN SINGLET OXYGEN AND IODINE MONOFLUORIDE

THESIS

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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

William M. Lee, B.S.

Captain, USAF

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Preface

This research is part of an on-going project at AFIT to better understand the energy transfer mechanisms between oxygen and interhalogen molecules. Specifically, chemiluminescent experiments were conducted to study the energy transfer mechanisms between singlet oxygen and iodine monofluoride. A solid understanding of the processes may allow researchers to develop an efficient high energy chemical laser system using these reactants.

I wish to thank Dr. Won B. Roh, my advisor, for providing critical guidance while allowing me the opportunity to develop and test my own ideas. His flexibility made this research both educational and enjoyable. I thank Dr. Earnest A. Dorko, at the Air Force Weapons Lab, for sponsoring this thesis. His continued support and interest provided motivation by helping me to realize the potential value of this research is more than simply an academic requirement for graduation. I am indebted to Captain Ray O. Johnson for the hours he spent pointing out the idiosyncrasies of the test equipment and teaching me the details of how he conducted his original experiment. I am especially grateful to Mr. Jimmy Ray for making countless glass components used in the experiments on very short notice. Finally, I wish to thank God for giving me a wife with the patience to endure these last 18 months.

William M. Lee

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Abstract

Chemiluminescence was observed from Iodine Monofluoride (IF) excited by singlet oxygen [$O_2(a^1\Delta)$ and $O_2(^1\Sigma)$] in a gas flow tube reactor as a means to study the O_2-IF energy transfer mechanisms. Although several researchers have demonstrated singlet oxygen's ability to efficiently pump IF(X) to the IF(B) state, the exact details of the processes have not been determined. The purpose of this research was to conduct IF(B) chemiluminescence spectral analysis and $O_2(^1\Sigma)$-quenching experiments to further define the excitation processes and to develop plausible mechanistic models based on experimental results. The spectral analysis revealed that the majority of the IF(B→X) transitions originated from the IF(B,v'=0) and IF(B,v'=1) energy levels. The $O_2(b)$-quenching experiments suggest that $O_2(b)$ is not critical in the excitation of IF(X) under the conditions of this research. Two plausible mechanistic energy transfer models were presented based on experimental results.

COLLISIONAL ENERGY TRANSFER MECHANISMS BETWEEN SINGLET OXYGEN AND IODINE MONOFLUORIDE

I. Introduction

Overview

The Air Force is interested in developing efficient high energy short wavelength chemical laser (SWCL) systems for spaceborne applications. A SWCL has not yet been demonstrated, but one promising concept is to use energy transfer from a chemically produced metastable atom or molecule to a suitable laser species. Singlet oxygen, O_2*, and iodine monofluoride, IF, has been investigated as possible candidates for the metastable molecule and lasant respectfully (1:1).

Durie, Whitefield, Shea, Davis, Johnson and others demonstrated that $O_2(a^1\Delta_g)$ is an efficient energy transfer agent for exciting ground state iodine monofluoride, IF(X), to the excited IF(B) state (1-5). Although these researchers hypothesized and experimentally tested different their models, the exact details of the processes have not been determined. Most researchers applied kinetic analysis to IF(B) chemiluminescent experiments to study the interaction between IF and $O_2(a^1\Delta g)$. This thesis more closely builds upon the experimental design and techniques

employed by Johnson. Modifications to Johnson's design include the use of quenching gases, different concentrations of reactants, flowmeters with a larger dynamic range, the addition of light traps, and miscellaneous other design changes. Details of the design and experimental procedures are presented in the applicable sections of this thesis.

Background

The lowest lying electronic excited states of oxygen, $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g)$ [hereafter designated as $O_2(a)$ and $O_2(b)$ respectfully], are metastable because they cannot dispose of their excess electronic energy due to selection rule prohibitions for optical dipole transitions to the ground state, $O_2(X^3\Sigma_g)$. In addition, $O_2(a)$ is also remarkably resistant to relaxation by collisions. These qualities combined with its ability to transfer its energy to other atoms or molecules, make $O_2(a)$ a primary candidate for chemical laser applications (6:103).

Concerning the laser species, Davis and others reported the radiative and collisional properties of $IF(B \rightarrow X)$ to be nearly perfect for chemical laser development. Davis summarized

> In addition to radiative lifetimes that offer large optical gains, the equilibrium internuclear separation for the B state is 10 percent greater than that for the X state. Consequently, the largest Franck-Condon Factors ($q_{v',v''}$) for $IF(B \rightarrow X)$ terminate on high v" (v" = 4,5,6) [1:1].

The termination on high ground state vibronic levels facilitates the formation of a population inversion without requiring a majority of the IF(X) molecules to be pumped to the IF(B) state.

Visible chemiluminescence of metastable oxygen pumped IF was first observed by Durie in 1951 and initiated investigations in using metastable oxygen and IF as possible sources for chemical lasers (7:6793). The search for a visible chemical laser continued on a subdued level until the formation of a national Strategic Defense Initiative renewed interest in developing high energy chemically pumped lasers. More recent additional chemiluminescent experiments further supported the notion of using metastable oxygen and IF for a SWCL system (1:1).

Problem Statement

The exact mechanisms by which metastable oxygen pumps IF(X) to the excited IF(B) state have not been conclusively determined. The purpose of this thesis is to design and conduct IF(B) chemiluminescent experiments to further define the excitation process, and to develop plausible mechanistic models for the energy transfer between $O_2(a,b)$ and IF based on experimental results.

Summary of Current Knowledge.

Variations in results due to different experimental conditions and methods, reactants, and vibrational states of

the molecules have hindered researchers attempts to identify the most efficient energy transfer mechanisms between metastable oxygen and IF(X). For example, Davis and others found that IF(B) is excited by two distinct processes depending upon whether vibrationally cold or hot IF(X) is used as the ground IF source (4:17). Whitefield, Shea and Davis also found a strong dependency of the IF(B) chemiluminescent intensity on the specific reactants used to form IF(X).

The Whitefield group studied singlet molecular oxygen pumping of IF by measuring the chemiluminescence generated from the following reactants: $I_2 + F_2$; $I_2 + F_2 + O_2(a,b)$; and $I_2 + F + O_2(a,b)$. The F atoms were formed by breaking F_2 molecules apart in a microwave cavity (estimated conversion efficiency of 70-80%). They reported

> The emission intensity produced by the $I_2 + F_2$ reaction was enhanced by approximately an order of magnitude upon the addition of 0.5 Torr of microwave excited O_2. (The discharge produced about 5% of the O_2 in the $a^1\Delta$ state.) The addition of fluorine atoms to the $O_2^* + I_2 + F_2$ flame produced approximately a fivefold additional increase in the IF emission intensity [8:6795].

Additionally, the Whitefield group performed an experiment which provided preliminary evidence that $O_2(b)$ was not primarily responsible for the excitation of IF(X) in tneir experiments and thus $O_2(a)$ was probably the excitation source (8:6797).

The T_e for IF(B) is 19054 cm^{-1} in contrast to the available energy of 7882 cm^{-1} for $O_2(a)$ (8:6797). Whitefield and others explain the significance of this energy difference

> Energetically, a minimum of three $O_2(^1\Delta)$ molecules would be required to promote an IF molecule from $X^1\Sigma(v''=0)$ to the $B^3\pi(0^+)$ state. This implies a sequential pumping scheme in which one energy transfer from $O_2(^1\Delta)$ leaves IF in some intermediate state [8:6797].

More recent research in IF chemical lasers was performed by Davis and others (1-4) under contract with the United States Air Force Weapons Laboratory (AFWL) and by LT Ray Johnson at AFIT (5). Both Davis and Johnson investigated ways of exciting IF using metastable singlet O_2. Their results are reviewed in the following paragraphs.

The Davis research team set out to determine if $O_2(a)$ could efficiently pump IF(B) by E-E transfer collisions and to investigate any possible roles of $O_2(b)$ in the excitation process. Because neither $O_2(a)$ nor $O_2(b)$ has sufficient energy to pump IF(X;v"=0) directly to IF(B), the Davis team believed sequential collisions involving IF(A'($^3\pi_2$)) as an intermediate energy reservoir in the IF manifold was required. Davis noted that although $O_2(a)$ cannot directly pump IF(X;v=0) to IF(A'), $O_2(b)$ may contain sufficient energy. However, if IF(X) is excited into a high enough ground state vibrational level, then $O_2(a)$ may have the required excitation energy (2:2). Thus, the vibrational

distribution of the IF(X) molecule is important for assessing plausible energy transfer mechanisms between metastable O_2 and IF.

The researchers used a flow tube reactor and measured the IF(B $\rightarrow$X) and O_2(b $\rightarrow$X) chemiluminescent intensities created from various precursors which formed IF(X) with different vibrational distributions. The following two reactions were among those used to produce IF(X)

$$CF_3I + F \rightarrow IF + CF_3 \quad (1)$$

$$I_2 + F \rightarrow IF + I \quad (2)$$

Previous work by Stein and Wanner showed that reaction (1) produced IF(X) with a vibrational distribution peak at v"=0 and rapidly diminishing such that essentially no IF(X,v">7) is produced (9:1128). However, reaction (2) produced a bimodal distribution with a peak at v"=0 and a relatively large population with v">10 (IF^+) (10:6091). Their results are presented in Figures (1) and (2).

Davis found the IF(B $\rightarrow$X) chemiluminescent intensity from the I_2 + F + O_2* reaction to be at least two orders of magnitude larger than that originating from the CF_3I + F + O_2* reaction. However, when the I_2 + F were mixed upstream (>5 ms) of the O_2*, the emission was much less intense and only a factor of two greater than the CF_3I + F + O_2* reaction. Davis suggests the IF(X) formed from I_2 + F precursors may have initially contained internal vibrational

energy which relaxed during the transient time of the IF(X) molecules to the O_2* injector. They labeled the vibrationally hot IF(X) as IF^+ (1).

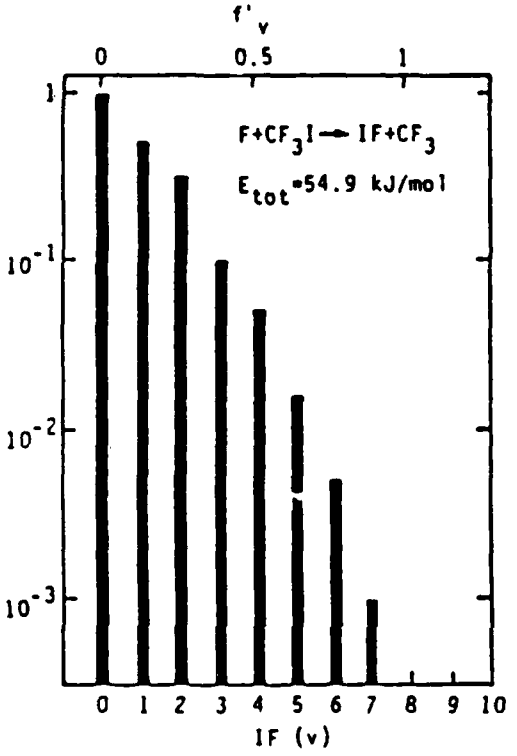

Figure 1. Detailed Rate Constants, k_v, for Partitioning of Vibrational Energy in IF(X) Formed from CF_3I + F (9:1128)

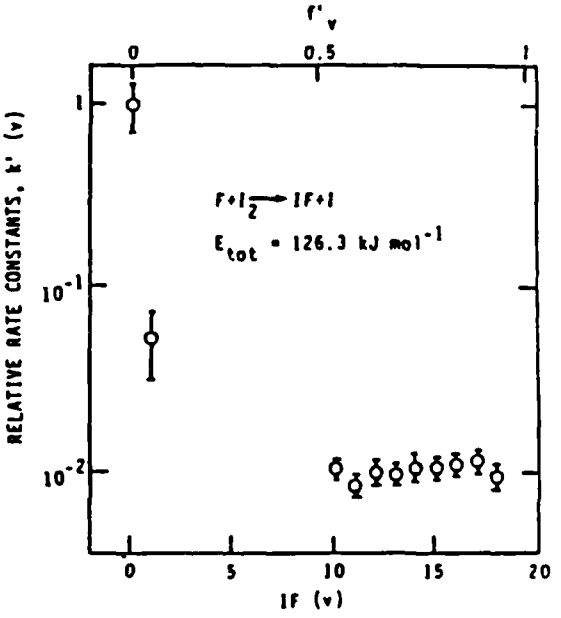

Figure 2. Detailed Rate Constants, k_v, for Partitioning of Vibrational Energy Formed from F + I_2 (10:6508)

Davis added O_2(b) specific quenching gases (CO_2 and H_2) to the IF(X) precursors formed from I_2 + F, I_2 + F mixed 9 ms upstream of the O_2* injector, and CF_3I + F precursors as a means to study the role of O_2(b) in the excitation. The quencher allows the researcher to vary the [O_2(b)] without substantially altering the [O_2(a)].

They monitored the chemiluminescence of both the $O_2(b \rightarrow X)$ and $IF(B \rightarrow X)$ as a function of the added quencher gas. Surprisingly, the [IF(B)] from the I_2 + F precursors increased as $O_2(b)$ was removed. However, when the I_2 + F was mixed upstream of the O_2^*, the IF(B) production efficiency was linearly dependent on the $[O_2(b)]$. Likewise, the chemiluminescence from the CF_3I + F precursors was strongly dependent on the $[O_2(b)]$. Their results suggest $O_2(b)$ is directly involved in pumping vibrationally cold IF(X), while $O_2(a)$ is the primary molecule for pumping IF^+.

The Davis group used laser induced fluorescence (LIF) studies to confirm that IF(B) was indeed excited by two distinct mechanisms (3:17). Detailed LIF showed that IF(B) production scaled linearly with IF(X,v">9) when $O_2(a)$ was the pump source. They presented two mechanistic models in their final report depending upon whether vibrationally cold or hot IF was involved in the excitation process (1).

Davis's cold IF model is summarized in equations (3) and (4)

$$IF(X,v''=0) + O_2(b) \rightarrow IF(A') + O_2 \quad (3)$$

$$IF(A') + O_2(a) \rightarrow IF(B) + O_2 \quad (4)$$

Davis's IF^+ model is summarized in equations (5) and (6)

$$IF^+ + O_2(a) \rightarrow IF(A') + O_2 \quad (5)$$

$$IF(A') + O_2(a) \rightarrow IF(B) + O_2 \quad (6)$$

Johnson used a flow tube reactor to generate IF(B) chemiluminescence from $CF_3I + F + O_2^*$ and he applied kinetic analysis to evaluate three proposed oxygen-IF energy transfer mechanisms (5).

His mechanism one is a 1-step process in which three $O_2(a)$ molecules simultaneously collide with ground state IF(X) to excite it to the IF(B) state.

Mechanism two is a 2-step reaction in which two $O_2(a)$ molecules pool their energy to form one $O_2(b)$ molecule. The $O_2(b)$ molecule then transfers its energy to IF(X) to raise it to an intermediate IF($A'^3\Pi_2$) state. A third $O_2(a)$ molecule reacts with the A' state to form IF(B).

Mechanism three requires a sequential pumping of IF(X) by two $O_2(a)$ molecules within the ground state IF vibrational manifold. Then, a third $O_2(a)$ molecule reacts with the vibrationally hot IF(X) to excite it into the IF(B) state.

Johnson's results suggested the sequential pumping of IF(X) by $O_2(a)$ (mechanism three) was the excitation process occurring under his experimental conditions (5:53).

Scope

This thesis will investigate $O_2(a,b)$ pumping of IF(X) created from the $CF_3I + F$ precursors. The vibrational distribution of the IF(X) molecules will be assumed to be comparable to those obtained by Stein and Wanner for their

CF_3I + F reaction (see figure 1). Quenching gases specific for $O_2(b)$ will be added to reduce the $[O_2(b)]$ in the system and the resulting effect on [IF(B)] will be evaluated in order to assess the role of $O_2(b)$ in the pumping reaction.

Approach

Reactants will be mixed in a low pressure flow tube reactor to form IF(B). A photomultiplier tube and monochromator will be used to measure and spectrally resolve the resulting chemiluminescence from the IF(B $\rightarrow$X) transitions. The spectrum will be plotted as a function of wavelength and the vibrational bands of the IF(B $\rightarrow$X) transitions will be determined.

After completion of the IF(B) chemiluminescence spectral analysis, an $O_2(b)$-specific quenching gas (CO_2) will be injected in the stream of $O_2(a,b)$ molecules as a means to assess the role of $O_2(b)$ in the energy transfer process. The intensity of the IF(B $\rightarrow$X) emissions will be monitored as a function of the increase in pressure due to the CO_2. Because the absolute quantities of the reactants cannot be determined and the IF(B) production may be perturbed by the increase in pressure and gas flow from the quenching gas, a control will be used to evaluate the results. A control gas with a low $O_2(b)$ quenching rate coefficient (helium) will be substituted for CO_2 and the quenching experiment reaccomplished. The difference in the

intensity of the IF(B) chemiluminescence (photon count) caused by proportional increases in the pressure from CO_2 compared to helium will be used to assess the role of $O_2(b)$ in the pumping reaction.

A final quenching experiment will be performed where CO_2 is injected in the $O_2(a,b)$ gas flow to reduce the photon count to about one-half of the initial value. The CO_2 flow will be incrementally replaced by helium so as to maintain the total pressure constant. The photon count will be recorded and the process repeated until the CO_2 totally replaces the helium. The difference in the intensity caused by the quencher versus the control gas will again be used to assess the role of $O_2(b)$.

Summary

The tremendous variation in the IF chemiluminescent intensity based on different experimental conditions, reactants, and IF(X) vibrational distributions, has complicated efforts to identify the most efficient energy transfer mechanism. This variation has caused researchers to obtain seemingly conflicting results. The dilemma is due in large part to different mechanisms and combinations of mechanisms, operating under diverse experimental conditions. For example, recall that Davis and others demonstrated two distinct primary excitation routes depending upon whether

vibrationally excited or cold IF was used as their ground state IF source (1).

Research must be continued to conclusively determine the primary mechanisms by which singlet oxygen transfers energy to iodine monofluoride under diverse experimental conditions. A solid understanding of the excitation process is critical to the development of an efficient high energy chemical laser system.

II. Theory

This chapter discusses the significance of the oxygen and iodine monofluoride potential energy levels as a means to assess excitation mechanisms. It is followed by an explanation of the energy transfer models which will be tested against experimental results.

Potential Energy of Oxygen and Iodine Monofluoride

The available energy the $O_2(a)$ and $O_2(b)$ molecules from $v'=0$ to $v''=0$ transitions is about 7882 cm^{-1} and 13121 cm^{-1} respectfully (11:560). The potential energy diagram for oxygen is illustrated in Figure (3). By contrast, the

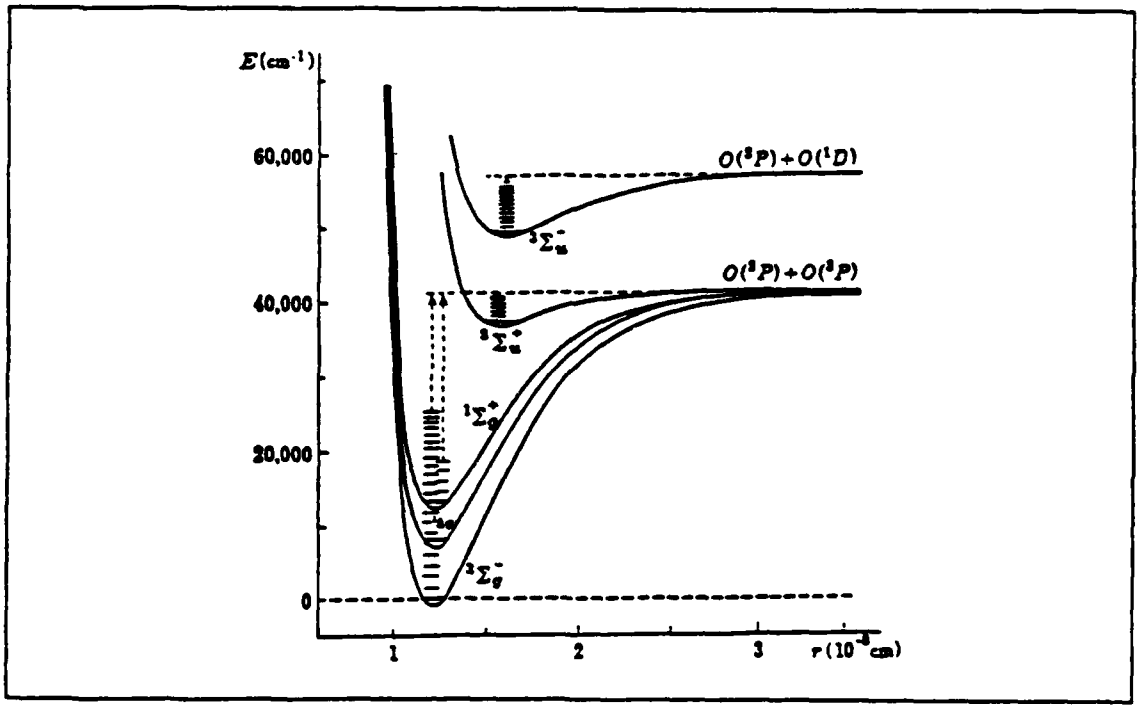

Figure 3. Potential Energy Diagram of O_2 (11:446)

energy required to excite IF(X,v"=0) to IF(B,v'=0) is approxima.ely 18,953 cm^{-1}. The potential energy diagram for IF is presented in Figure (4).

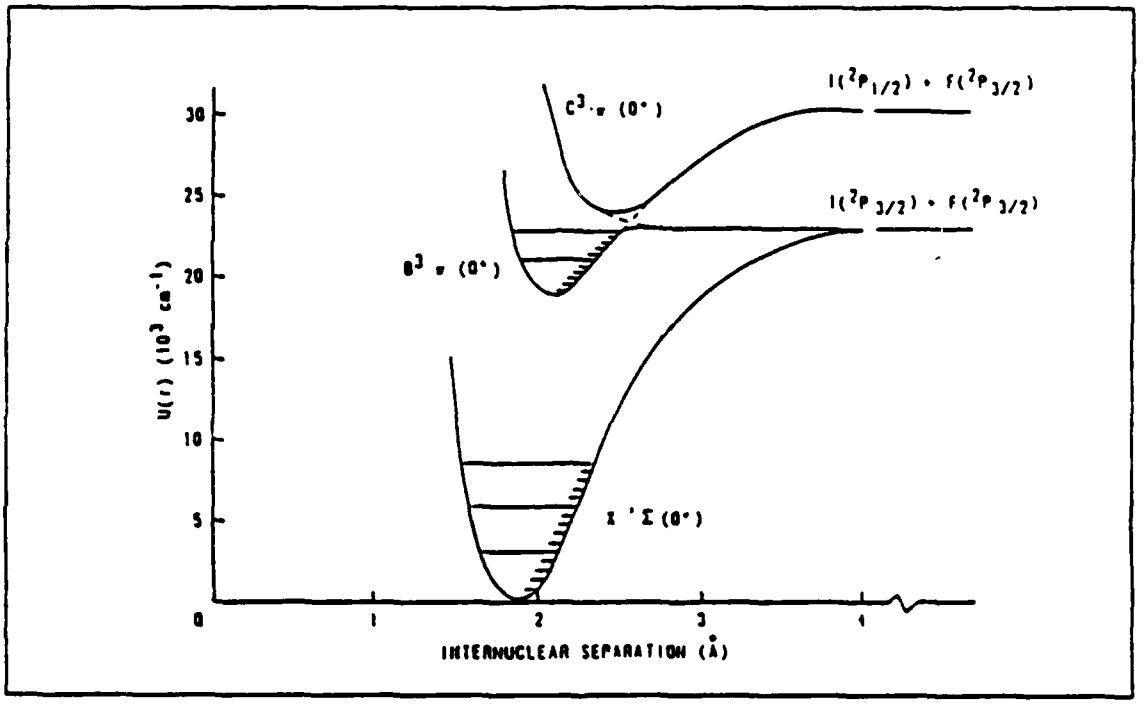

Figure 4. Potential Energy Diagram of IF (12:3)

The minimum number of singlet oxygen molecules needed to provide sufficient energy to excite IF(X) to IF(B) state depends on the initial energy level of the IF(X) molecule, the intermediate IF state, and the type of singlet oxygen molecule [O_2(a) or O_2(b)] operative in the transfer. A combined schematic diagram of the IF and O_2 molecules is presented in Figure (5).

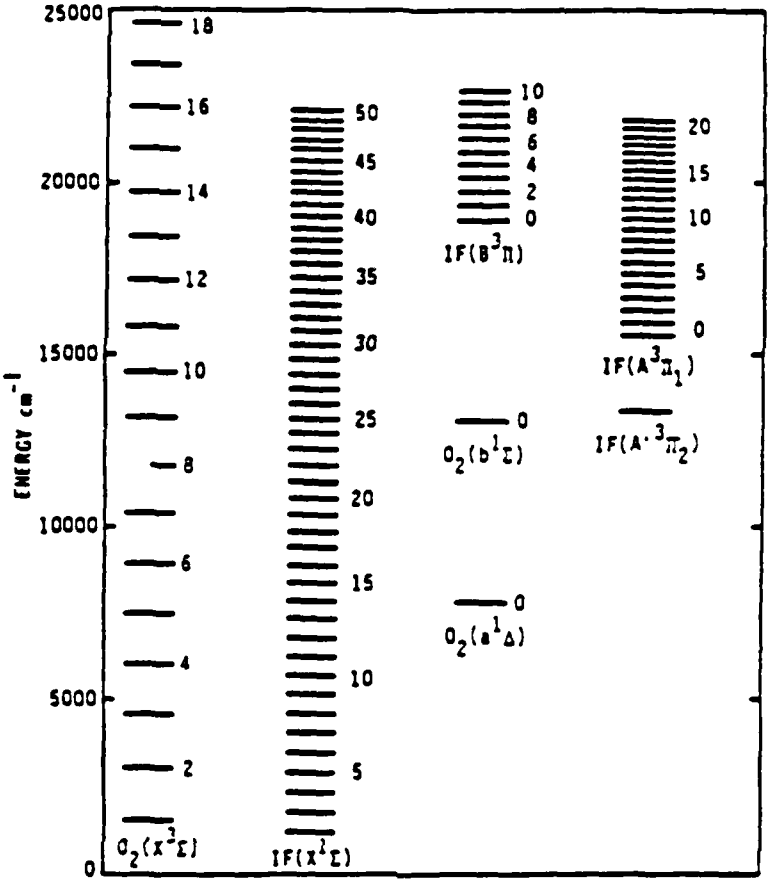

Figure 5. Energy Level Diagram of IF and O_2 (1:26)

Excitation Models

The energy transfer mechanisms presented by other researchers and explained in chapter one of this thesis are used as the basis for the selecting models which will be tested against experimental results. A brief discussion of the rational behind selecting the models will be discussed.

According to the Davis groups' criteria, IF(X,v"<9) is considered vibrationally cold. Because the IF(X) precursors used in this research do not produce significant quantities of hot IF(X), Davis's cold IF model will not be tested.

Johnson's mechanism one requires a four body collision (5). Due to the small probability of this occurring under the low pressure conditions of this research, his mechanism one will not be considered. If the $O_2(b)$ generated from the microwave discharge in this research is mainly formed by the energy-pooling of 2 $O_2(a)$ molecules ($k = 2 \times 10^{-17}$ cm^3-sec^{-1}) as determined by Derwent and Thrush and reported by Setser (13:204), then Johnson's mechanism two can be treated as Davis' cold IF model and will be tested against experimental results. Johnson's mechanism three involves the sequential pumping of IF(X) within its vibrational manifold by $O_2(a)$ molecules until it is electronically excited into the IF(B) state. Because Johnson's results suggested mechanism three is operative, it will also be tested against results from this research.

From a conservation of energy standpoint, one final mechanism is plausible. The IF(X) precursors used in this research produce a small population of IF(X,v"=6 and v"=7) (9:1128). Sequential pumping of IF(X,v"=6,7) by two $O_2(a)$ molecules could provide the necessary energy to pump IF(X) to the IF(B) state. Therefore, if the IF(X) is formed sufficiently close to the reaction chamber, then a small fractional population of the IF(X) molecules may contain enough ground state energy to allow excitation by only two $O_2(a)$ molecules. In addition to reducing the minimum number of $O_2(a)$ molecules required for excitation, the internal

energy of vibrationally excited IF(X) molecules also alters the vibrational wave function of the molecule. For these reasons, it will be considered as a separate mechanism.

In summary, three excitation schemes will be considered. The first mechanism is from Davis's cold IF(X) model. The second is Johnson's IF(X) vibrational manifold model. And finally, the third mechanism considers the possibility of IF(X,v"=6,7) being important components. All three models are outlined below. The symbol ">" indicates additional vibrational energy increments on the order of an $O_2(a \rightarrow X)$ transition (7882 cm^{-1}).

Model 1.

$$O_2(b) + IF(X) \rightarrow IF(A') + O_2(X) \quad (7)$$

$$O_2(a) + IF(A') \rightarrow IF(B) + O_2(X) \quad (8)$$

Model 2.

$$IF(X,v"=0) + O_2(a) \rightarrow IF(X,v">0) + O_2(X) \quad (9)$$

$$IF(X,v">0) + O_2(a) \rightarrow IF(X,v">>0) + O_2(X) \quad (10)$$

$$IF(X,v">>0) + O_2(a) \rightarrow IF(B) + O_2(X) \quad (11)$$

Model 3.

$$IF(X,v"=6,7) + O_2(a) \rightarrow IF(X,v">6,7) + O_2(X) \quad (12)$$

$$IF(X,v">6,7) + O_2(a) \rightarrow IF(B) + O_2(X) \quad (13)$$

III. Experimental Apparatus

Introduction

This section describes the experimental apparatus used in this research. A schematic diagram for the subsystems are presented in figures (6) and (7). The two major subsystems are the flow tube reactor for generating IF(B) and the optical analysis and recording system for measuring and recording the spectrum. Both of these major subsystems are discussed in the following sections.

Flow Tube Reactor System

The flow tube reactor consists of the following components:

(1) Flowmeters

(2) Plumbing and Reactants

(3) Vacuum

(4) Six-Way Cross (Reaction Chamber)

Figure (6) is a schematic diagram of the flow tube reactor system. A discussion of the construction of each of the system components is also presented.

Flowmeters. The reactant and quenching gases are fed into the flow tube system through one of two different size Airco flowtubes (SS754 and SS756) depending upon the required flow rates for the specific gases. Each of the flowtubes contains both a glass and stainless steel metering ball (float) to allow metering over a large dynamic range.

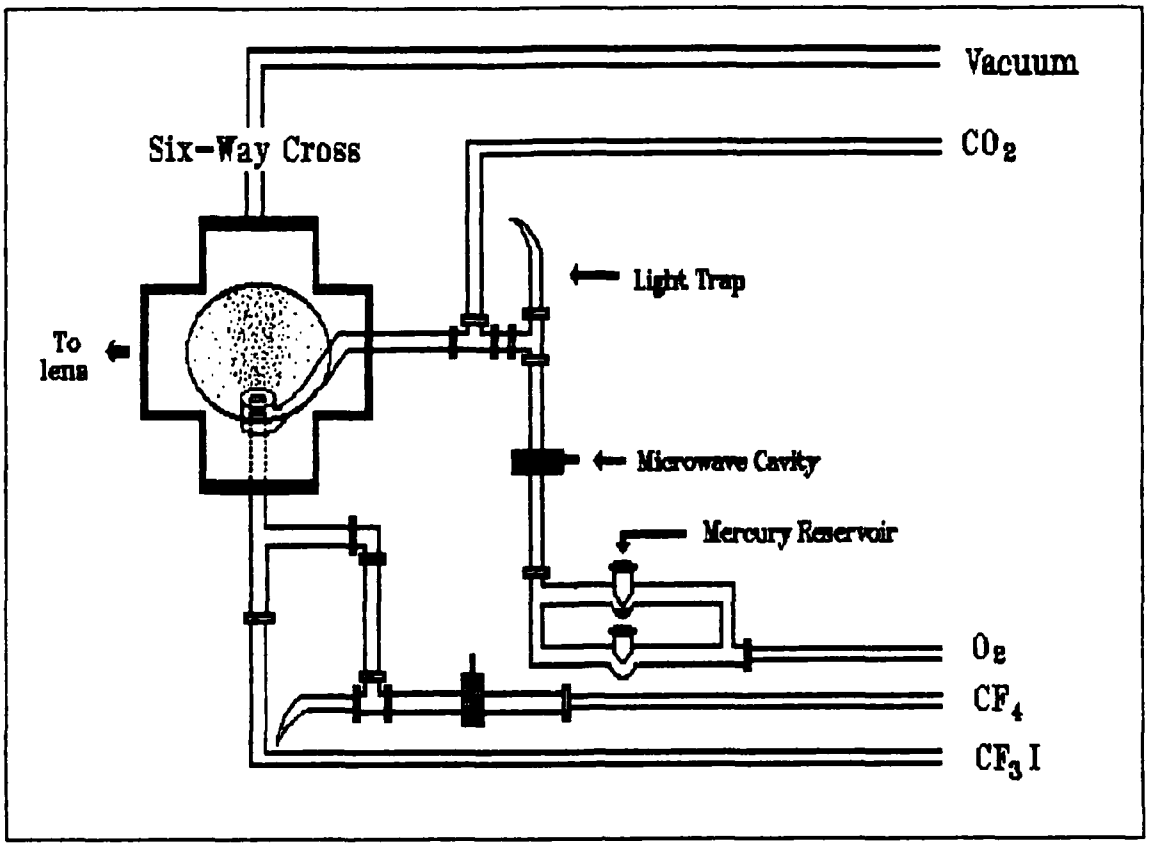

Figure 6. Schematic Diagram of Flow Tube Reactor System

The SS754 tubes are designed to meter flows from 0.0423-0.820 SCFH for the glass float and 0.0847-1.82 SCFH for the stainless steel float. The SS756 tubes have dynamic ranges of 0.212-5.10 SCFH for the glass float and 0.424-10.2 SCFH for the stainless steel float. Although CF_3I is the only gas requiring the smaller SS754 tube due to its low flow rate, O_2 is also controlled better with the smaller tube. The flowmeters provide a coarse indication of the relative proportions of gases and thereby facilitate the production of IF(B); but, the tubes are not calibrated sufficiently for kinetic analysis.

Plumbing and Reactants. The gas supply cylinders are connected to the flowmeters by 1/4 inch outside diameter (OD) copper tubing. The gas lines exiting the flowmeters also use 1/4 inch tubing to transport the gas to the other flow tube components necessary for the production of IF(B). Swaglock connectors are primarily used to join metal-to-metal tubing and Cajon connectors are used whenever glass or ceramic lines are incorporated in the system. Each of the low pressure gas line components (see Figure 6) will be discussed below.

The oxygen line connects to a 1/2 inch OD glass dual valve system immediately prior to the microwave discharge cavity. One branch of the dual valve system contains a reservoir of mercury. When the mercury branch is open, mercury vapor flows through the microwave cavity and creates a mercuric oxide ring on the oxygen inlet tube. This mercuric oxide coating removes atomic oxygen, a known quencher of IF(B), from the flow tube system (14:11). The mercury branch is closed during actual experimental recordings to prevent the mercuric oxide from migrating into the mixing bowl. The mercury branch is only opened before subsequent experiments whenever the mercuric oxide coating becomes depleted.

The oxygen next passes into a 1/2 inch OD aluminum oxide tube where it is exposed to a 120 Watt-2450 Mhz microwave cavity. The microwave discharge converts from 5-

15% of the molecular oxygen into the excited $O_2(a)$ state and a much lower percentage into $O_2(b)$ (13:204). The cavities are stabilized using a liquid-N_2-cooled N_2 gas circulated through the cooling port of the cavities to prevent them from over-heating (15). The gas is cooled by flowing N from a high pressure cylinder through a dewar of liquid N_2. It is then transported through plastic tubing to the microwave cooling port.

A light trap is installed after the microwave cavity to prevent light (noise) generated by the cavity from interfering with the IF(B) emissions. A cardboard barrier was also erected between the flow tube reactor and the optical analysis system to further reduce the microwave cavity noise.

The microwave excited oxygen travels through a 1/2 inch OD copper tube until it reaches the reaction chamber and is injected from a glass mixing bowl into a stream of IF(X).

IF(X) is formed from CF_4 and CF_3I precursors. CF_4 is passed through a microwave discharge cavity and routed passed a light trap similar to the oxygen configuration. The microwave discharge breaks CF_4 into CF_3 radicals and fluorine atoms. These component gases are mixed with CF_3I in a halocarbon coated quartz glass tee immediately below the reaction chamber. The fluorine atoms react with CF_3I molecules to form IF(X) and CF_3 (9:1128). The halocarbon wax helps prevent IF(X) from breaking down into non-

functional and undesirable molecules (5:37). Ground state IF travels up the glass tube into the base of the oxygen inlet mixing bowl where it reacts with singlet oxygen to form IF(B).

Vacuum. The flow tube system is evacuated by a Sergeant-Welch, Model 1375 vacuum pump with a free-air displacement capacity of 1000 liters/minute. A large ball valve at the input to the pump is used to control the pumping rate. A cold trap constructed of 1/2 inch OD copper tubing submersed in liquid nitrogen was initially installed to reduce corrosive vapor contamination of the pump. The cold trap was later removed from the system because it became saturated with condensate over the course of the experiment and seriously degraded the pump's performance.

Six-Way Cross. The six-way cross is where the chemiluminescent flame is focused and is the heart of the reaction chamber. The left and front ports have plexiglass windows. The left window faces the monochromator and provides access to the flame for measuring its intensity. The front window serves as a viewing window for the researcher to observe the flame. The remaining four ports are covered by stainless steel plates with 1/2 inch Cajon feed-through connectors for joining flow tube reactor components. The top port provides access for the vacuum pump. The bottom port is for the IF(X) inlet tube and the

right port is for the oxygen and quenching gas inlet tube. The rear port provides access for a Baratron pressure gauge.

Optical Analysis and Recording System

A schematic diagram of the optical analysis and recording system is presented in Figure (7).

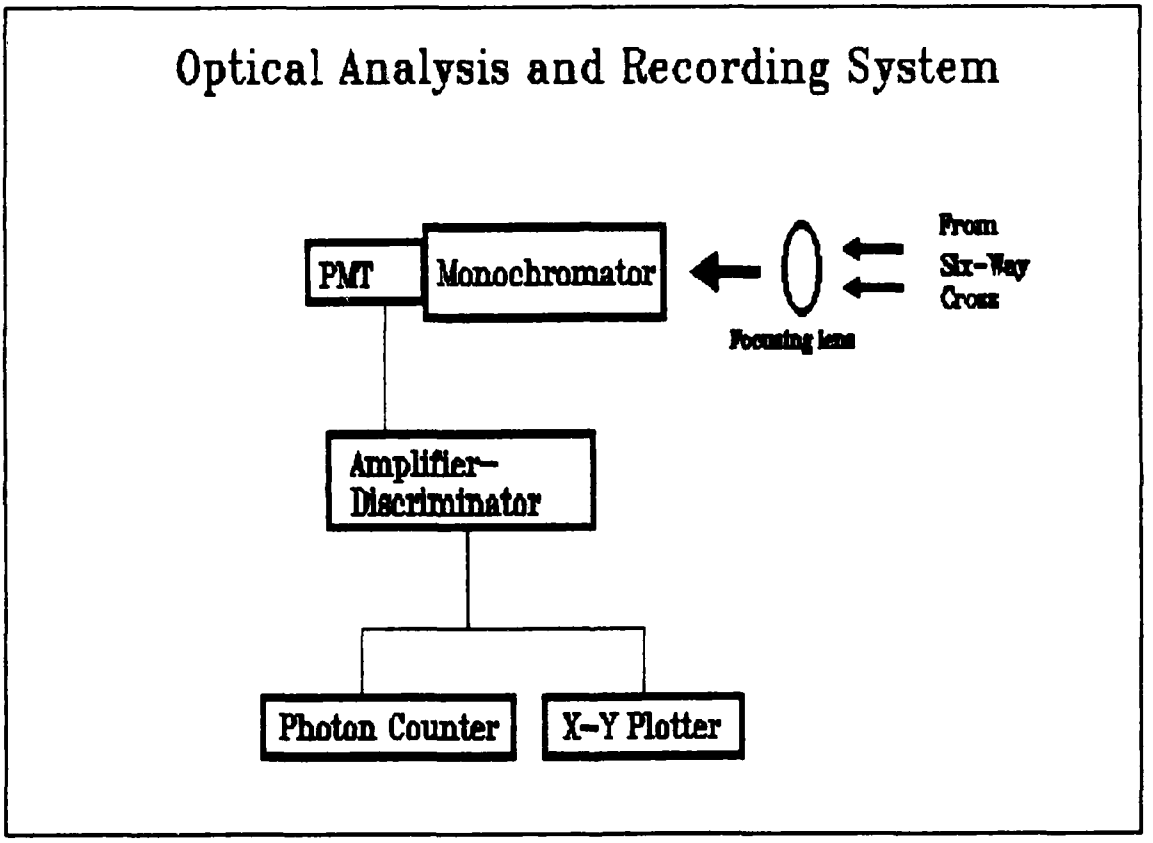

Figure 7. Schematic Diagram of the Optical Analysis and Recording System.

The chemiluminescence from the IF flame is collected by a 15 cm focal length glass collecting lens and focused onto the entrance slit of a 0.3 meter McPherson scanning monochromator. The monochromator exit slit is connected to

an RCA C31034-02 photomultiplier tube (PMT) contained in a thermoelectrically refrigerated chamber. The PMT has a gallium arsenide photocathode with a spectral response range from 250 to 850 nm.

The output of the PMT is sent to an EG&G Princeton applied Research Model 1121A Amplifier-Discriminator (photon counting system). The Amplifier-Discriminator supplies the bias voltage to the PMT and controls the signal threshold level to obtain a good signal-to-noise ratio. The Discriminator Control Unit (DCU) module of the Amplifier-Discriminator has both a digital and a positive analog voltage output. The digital output provides count data to an EG&G Model 1112 Photon Counter/Processor. The positive analog output voltage varies linearly with the count rate and is connected to a Soltech strip chart recorder.

The photon counter is set to display the photon counts per second detected from the IF(B) flame at the spectral location selected by the monochromator. The count readout is digitally displayed on the front of the photoncounter with light-emitting-diodes and is updated automatically for every one second time interval.

The X-Y plotter records the relative chemiluminescent intensity of the IF(B) flame as the monochromator scans the spectrum. A 50 micro Farad capacitor is installed between the positive and negative signal inputs of the recorder to help reduce the noise.

IV. Experimental Procedures

This section details the experimental operation and data collection procedures for the IF(B) chemiluminescence spectral analysis and quenching experiments. The general procedures common to all experiments will be discussed first. It is followed by procedures unique to the specific experiments.

General Procedures

The system is initially pumped to near zero torr (0.05-0.15 torr). The pump valve is closed and the pressure gauge monitored to verify that a vacuum leak does not exist in the flow tube reactor system. After the vacuum integrity of the system is established, the pump is opened slightly prior to flowing the reactant gases.

The O_2 and CF_4 flowmeters are opened to the rates experimentally determined from earlier trials. Initially the O_2 flow causes the pressure to increase to approximately 0.5 Torr. About 1.5 Torr of CF_4 is added bringing the total pressure to 2.0 Torr. Later in the experiment, after the flame is created, these flow rates will be fine tuned according to specific experimental objectives.

The microwave cavities are ignited after the gas flows and pressure readings stabilize. This is accomplished by switching on the high voltage power supply to one of the cavities, tuning the cavity to reduce the reverse power, and

exciting it with a tesla coil. After the cavity is lit, it is fine tuned until the reflected power reading on the 120 W-2450 Mhz power supply is between 0-3 Watts. Supercooled N_2 is circulated through the cooling port of the microwave cavity to prevent it from over-heating. Even though the ceramic tubing transporting the reactant gas becomes very hot over the course of an experiment, as long as the N_2 flow is sufficient to cool the metallic cavity, it remains stable for indefinite periods of time. Approximately 1500 psi of N_2 from a nitrogen cylinder is required to stabilize both cavities for a three hour experiment. The same procedure is repeated to ignite and stabilize the remaining microwave discharge cavity.

A relatively small flow of CF_3I is added to generate the IF(B) chemiluminescent flame. The flame may be fine tuned to the desired experimental condition by individually adjusting the flow rates for each of the component gases and vacuum pump. The oxygen inlet tube may need to be coated with mercuric oxide prior to collecting experimental data (refer to Chapter III for details).

IF(B) Chemiluminescence Spectral Analysis Experiments

The monochromator is initially set with a 2.0 mm slit width tuned near the bandcenter of the IF(B,v'=0) to IF(X, v"=4) transition (603 nm). This setting provides the maximum S/N ratio and is used when adjusting the flame.

The background count is determined by recording the photon counts prior to flowing CF_3I. Typical background counts are usually between 10-15 counts/second. Similarly, dark counts of 5-10 counts/second is determined by completely closing the shutter to the monochromator entrance slit and recording the readings.

The flame is created initially according to the instructions in the general procedures section of this thesis. The flame is then fine tuned for maximum photon count by individually adjusting flow rates of the component gases and vacuum pump.

By very gradually closing the pump and adjusting the flow rates, photon counts greater than 600/second can consistently be obtained. Thus, for the particular bias voltage and threshold setting of the detection system, a S/N ratio of 60 is easily obtained. Highest counts occur with pressure readings between 4.0 and 6.0 Torr.

The monochromator slit width is reduced to the desired setting and tuned to the upper wavelength location for the desired spectral scan.

The X-Y plotter's paper speed is selected at typically 2 or 4 cm/min. The plotter is started with the mode selected to record the zero position (no signal) of the plotter. This produces a straight line on the paper corresponding to the plotter's zero axis. The automatic scan of the monochromator is started toward the lower

wavelengths at a 10 nm/min scan rate. The plotter's mode is switched from "zero" to "on" while the researcher notes the displayed wavelength reading on the monochromator.

Because there is a 10 mV dc offset in the rate output of the DCU (input to the plotter), switching the plotter to "on" produces a vertical displacement on the paper and helps the researcher to establish the spectral scale on the plot. At the end of the spectral recording, the monochromator reading is again noted while simultaneously switching the plotter back to the "zero" position to provide a second vertical reference line on the paper.

For more precise spectral identification, the above described spectral recording procedure is repeated with Oriel pen lamp emissions scattered into the view window of the six-way cross. The superposition of the pen lamp's atomic transitions with IF(B) emissions provides a means to calibrate the plots. It was found that very little calibration is required for any of the direct monochromator readings. Calibration corrections varied from 0.0 to 0.5 nm depending on the specific monochromator spectral location and slit-widths used.

Quenching Experiments

Both the CO_2 and helium lines are evacuated prior to commencing the experiment. The flow tubes are then closed off to isolate the gas lines from the vacuum system. The

CO_2 and helium cylinders are opened to provide a slight positive pressure in the lines between the cylinders and flowtubes to insure air does not leak into the system.

The monochromator slit width is set at 2.0 mm and it is tuned to the v'=0 to v"=4 transition (603 nm).

The IF(B) flame is generated according to the instructions in the general procedures section. However, unlike the spectral resolution experiments, the vacuum pump valve is not closed to increase the pressure in the reaction chamber and thereby the maximum count. Instead, the pump valve is left open wider to allow the pressure to stabilizes at slightly above 2.10 Torr. This forces a higher flow rate of gases through the system and thus increases the responsiveness of the system to changes in gas flow. The component gas flow rates may require a slight adjustment to increase the photon count under these high flow rate conditions.

The control run is conducted first. The pressure and six readings of photon counts per one second time interval are recorded prior to adding helium to the system. A small quantity of helium is added and after the system stabilizes, the pressure and another group of photon counts are recorded. This process is repeated until the pressure reaches about 4.0 Torr. At around 4.0 Torr, the reverse power on the microwave cavities begins to rise. Rather than

risk non-uniformly retuning the cavities between subsequent experimental runs, the researcher stopped taking data point.

Once the helium control data is collected, the helium flow is halted and the system allowed to stabilize. In a few minutes, the photon count and reverse power on the microwave cavities return to approximately the original conditions prior to the addition of helium to the system.

The CO_2 gas flow is substituted in place of helium and the same procedure is repeated.

A second and slightly modified experimental run was performed at a later date. This time, a small quantity of desiccant was placed inside a "U-shaped" tube installed in the quenching line just prior to mixing with the oxygen flow. This was done to investigate the possibility of moisture in the CO_2 or Helium gases biasing the data. H_2O is known to be a strong quencher of $O_2(b)$. The pumping rate is increased and the photon count subsequently reduced to minimize the likelihood of any residual helium remaining in the low pressure lines and affecting the CO_2 results.

One final quenching experiment is performed where CO_2 is added to the system such that it reduces the count to less than one-half of the initial value. The CO_2 flow is gradually lowered while proportionately increasing the helium flow rate so as to maintain the pressure constant. The photon count is recorded and the process is repeated until the CO_2 flow has been totally replaced by helium.

V. Results And Discussion

Spectral analysis of IF(B) chemiluminescence and two types of quenching experiments were conducted and are discussed in the following sections.

IF(B) Chemiluminescence Spectral Analysis

Spectral scans of the IF(B) emissions were taken at various monochromator slit widths over a two week period. The spectral scans taken at slit widths of 1.0 mm and 0.6 mm provided the best compromise between separating vibrational bands within the IF(B $\rightarrow$X) electronic transitions and loosing the signal in the background noise.

The scans taken at 1.0 mm and 0.6 mm slit widths are presented in figure (8). The 1.0 mm scan shows relatively large amplitude peaks, but there is some overlap between adjacent transition with close bandcenters. The amplitude of the peaks in the 0.6 mm slit width scan are reduced, but the resolution is noticeably improved.

Because thermalization of IF(B) can dominate other processes (1:2), the relative amplitudes of the electronic transitions originating from particular IF(B) vibrational levels may not be indicative of the energy level's importance in the excitation process. For this reason, special effort was placed on identifying even the smaller transitions.

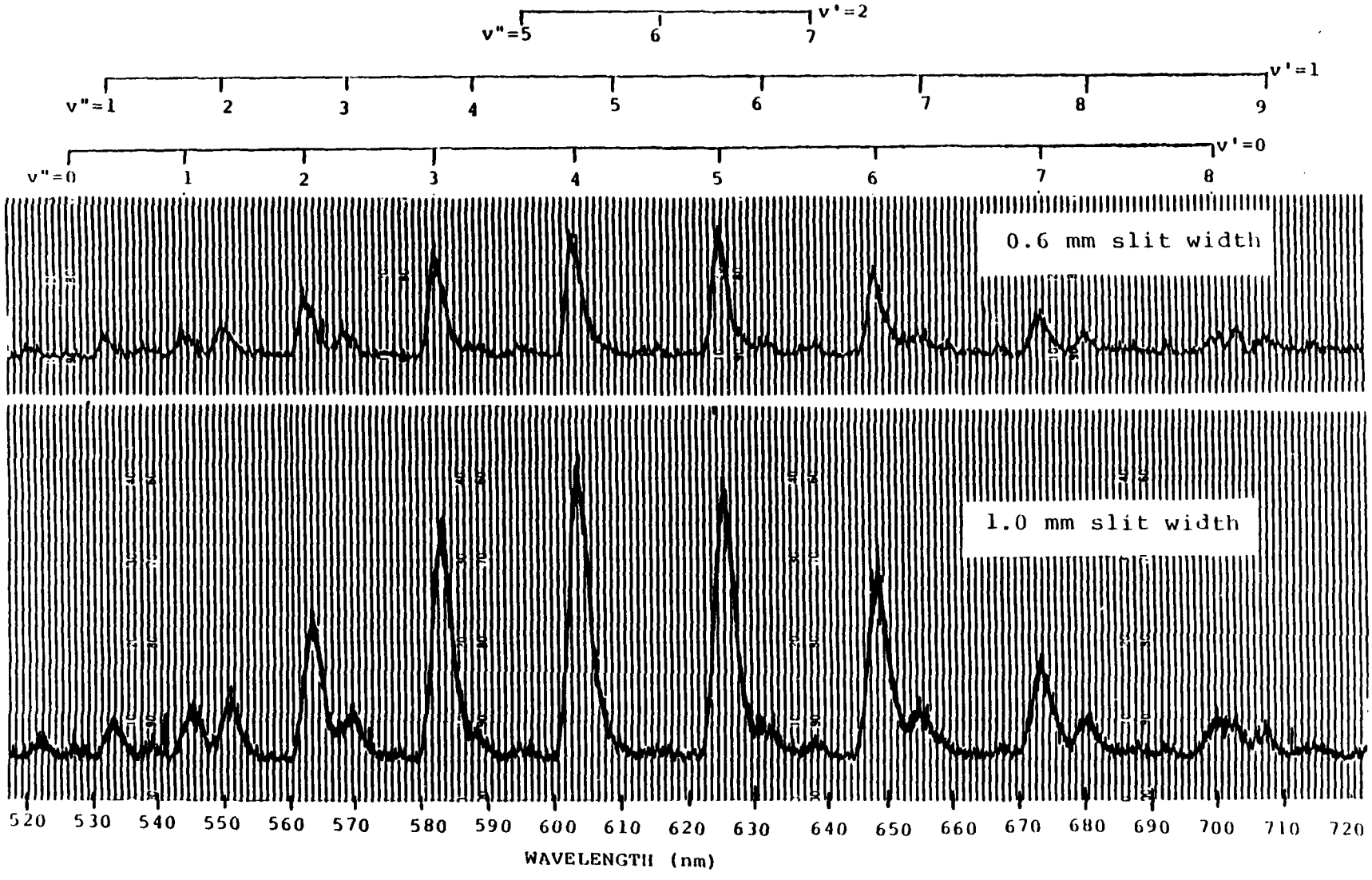

Figure 8. IF(B → X) Chemiluminescence Spectrum

Transitions from IF(B,v'=0,1) to a series of IF(X) levels ranging from (v"=0-9) are clearly shown and account for practically all the IF(B) chemiluminescence generated in this research. Much weaker peaks from (v'=2) to (v"=5,6,7) seem to be present in both scans. There also appears to be two small peaks centered near 667 nm and 692 nm in both scans. Although conclusive identification of these peaks cannot be made, it is possible that they correspond to the IF(B $\rightarrow$X) transitions of (6,11) and (6,12). Model 1 presented in this thesis requires an $O_2(a)$ molecule to transfer its energy to an intermediate IF(A') state and could provide sufficient energy to populate the IF(B,v'=6) energy level. If these transitions do indeed originate from v'=6, then this would be consistent on a conservation of energy standpoint with Model 1 excitation occurring.

It is also interesting to note that some of the transitions terminate in the (v"=6,7,8,9) levels. Under slow flow conditions, these molecules may become available for a second excitation by two $O_2(a)$ molecules (Model 3) and subsequently emit a second photon within the reaction region.

In summary, the majority of the chemiluminescent intensity comes from low-lying v' levels and practically no transitions were strongly correlated with IF(B,v'>2) levels. If the IF(B) molecules were highly excited, even with thermalization of IF(B) by other molecules, one would expect

to see some evidence of transitions occurring from high lying IF(B) vibrational levels. Thus, the IF(B) spectral analysis results suggests that IF(A') molecules are not important in the energy transfer processes observed under these experimental conditions.

Quenching Results

The purpose of the quenching experiments is to assess the role of $O_2(b)$ in the pumping of IF($X \rightarrow B$). Two types of quenching experiments were conducted. For the first type of experiment, the quencher (CO_2) was added causing the total pressure to increase while the IF($B \rightarrow X$) chemiluminescent intensity was recorded as a function of pressure. For the second type, the IF($B \rightarrow X$) intensity was first reduced by adding CO_2 and then the intensity was recorded as the CO_2 was incrementally replaced with a control (helium) such that the total pressure remained constant.

Increasing Pressure Quenching Experiment Data were collected for two slightly different experimental runs of the "increasing pressure" quenching experiments. The differences in the experiments and the results are reviewed in the following paragraphs.

The first experimental run used slower vacuum and gas flow rates and produced a relatively large initial S/N ratio of about 30 prior to adding the quenching gases. It was

conducted using unevenly spaced partial pressure additions of the quenching/control gas.

Data from the first experimental run are graphed in Figure (9). An experimentally determined background count of 10 was subtracted from the total count prior to plotting results. Because the initial count (prior to flowing the control/quenching gases) stabilized at a slightly higher count after completion of the helium flow, the data are normalized to the percentage of initial photon counts/second for comparison purposes.

The reaction chamber pressure was increased by adding incremental additions of control or quencher (depending on the portion of the experiment being conducted). The logarithm of the percentage of the initial photon counts per second are plotted as a function of reaction chamber pressure. There is no statistically significant difference between the effects caused by the quencher and that of the control.

The IF(B,v'=0) to IF(X,v"=3,4,5) transitions were plotted prior to adding helium or carbon dioxide to the system and after the intensities were reduced to less than one third of the original amplitudes. A comparison of the initial and final plots are shown in Figures (10) and (11). There does not appear to be any shift in the relative distributions caused by either of the gases.

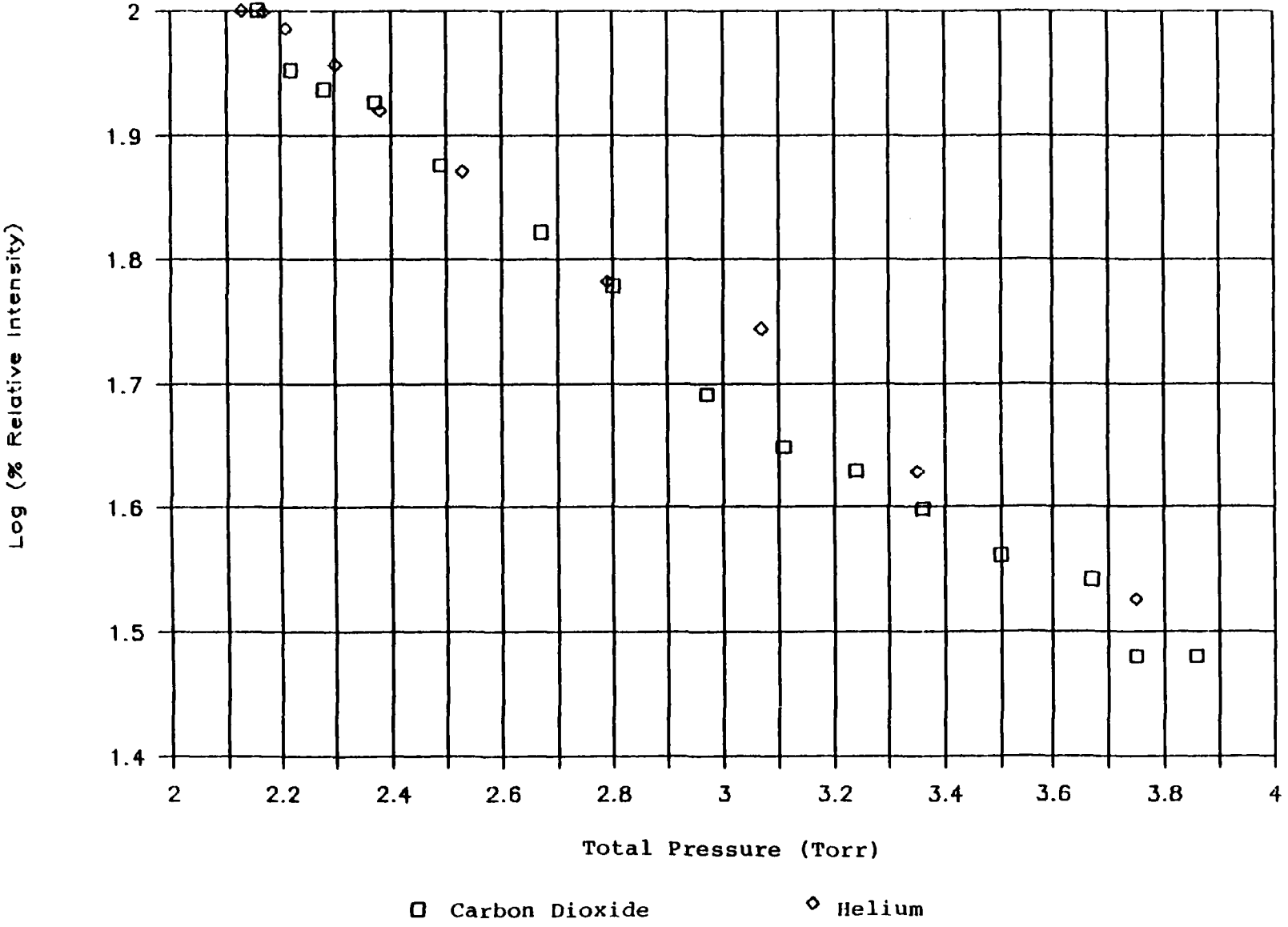

Figure 9. Relative Intensity of the IF(B,v'=0) to IF(X,v'=4) Transition as a Function of Total Pressure, Run #1

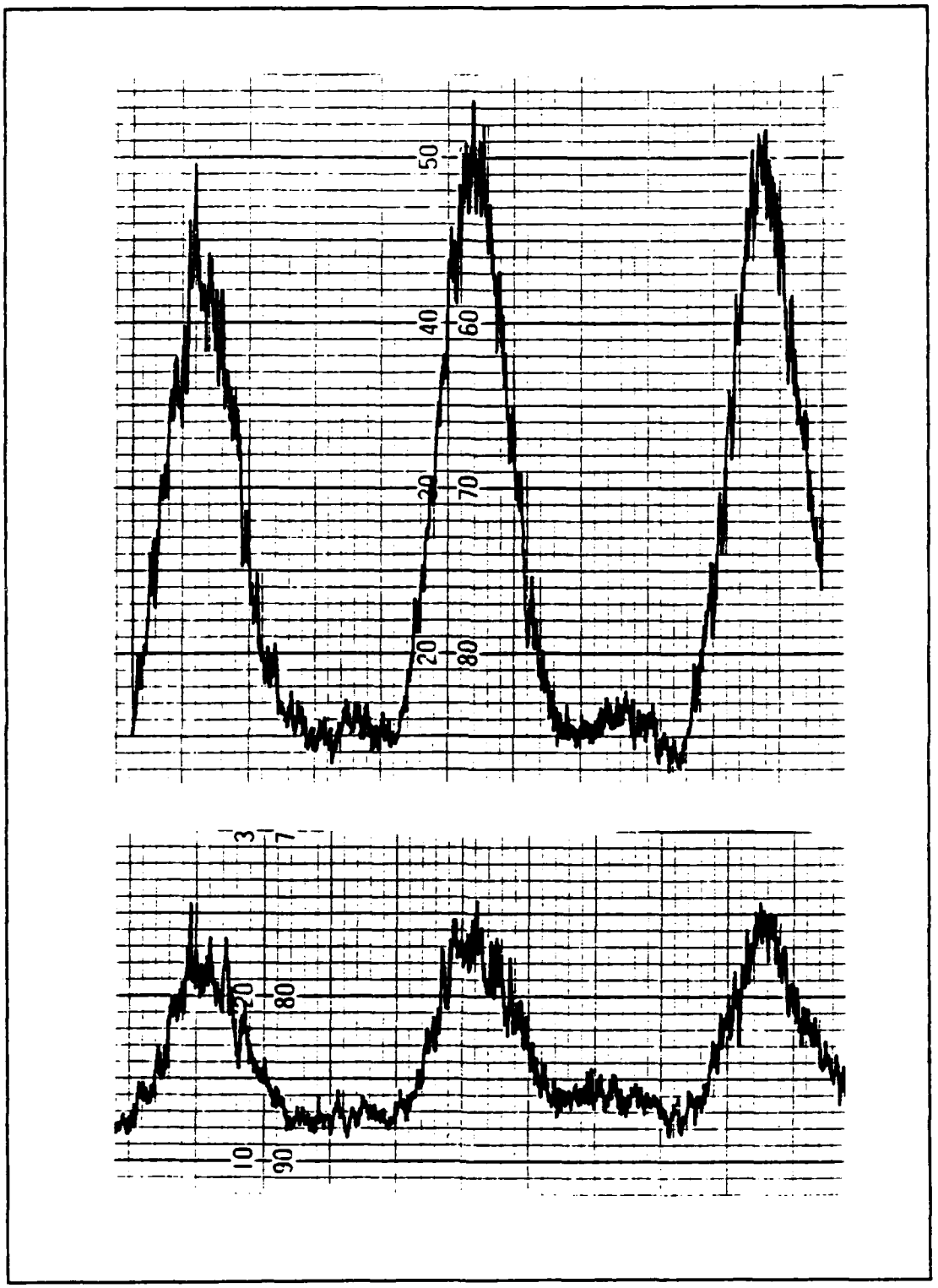

Figure 10. Comparison of the IF(B,v'=0) to IF(X,v"=3,4,5) Transitions Before and After Adding Helium to the System.

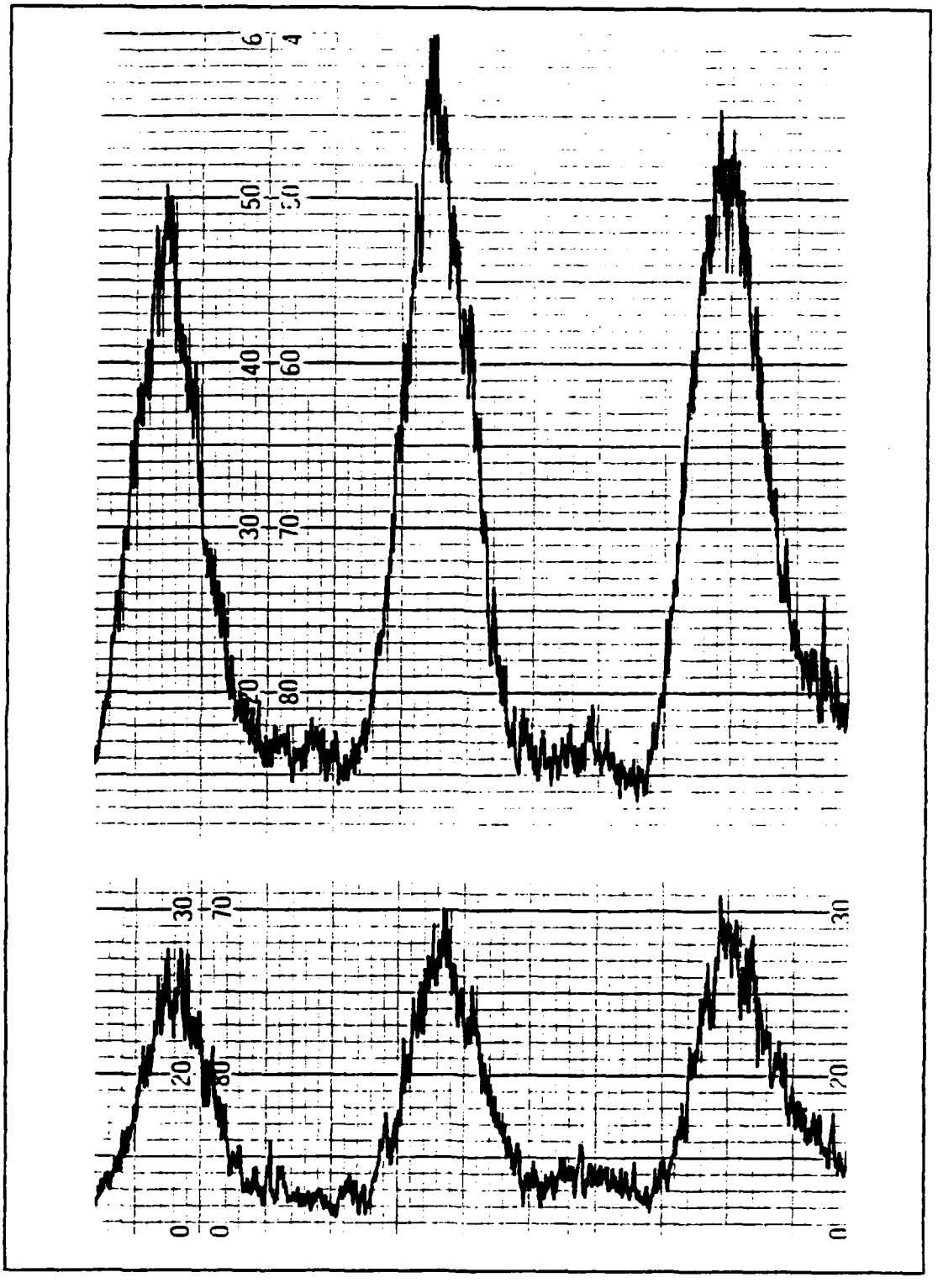

Figure 11. Comparison of the IF(B,v'=0) to IF(X,v'=3,4,5) Transition Before and After Adding Carbon Dioxide to the System.

A second slightly modified experimental run was conducted with faster gas flow rates, desiccant added in the quenching line, and evenly spaced partial pressure additions of the gases.

The vacuum pump and gas flow rates were increased to make the system more responsive. This was intended to help insure the quenching line was purged of residual helium prior to starting the CO_2 flow and to minimized the effects "shaping" of the chemiluminescent flame had on intensity measurement. The trade-off for the improved responsiveness was an over 60% reduction in the initial chemiluminescence intensity.

The desiccant was added to reduce the possibility of water from the helium cylinder biasing the results. Helium used in the experiment was high purity (99.995%) and the incorporation of the desiccant did not appear to alter experimental results. One should use the desiccant cautiously. Too much desiccant in the system may cause small quantities of the helium to become temporarily trapped in the system and subsequently released at a later time while flowing CO_2. Obviously, depending on quenching efficiencies and concentrations, this could bias experimental results.

The evenly incremented data points were slightly more difficult to obtain because it required the researcher to

fine tune the control/quenching gas flow rates; however, it simplified the data analysis and was worth the effort.

Results for the second experiment are graphed in Figure (12). Because the initial counts prior to adding the control and quenching gas were approximately the same magnitude, the counts were not normalized. Instead, the logarithm of the counts are plotted as a function of pressure in the reaction chamber. As found in the first quenching experiment, there is no statistically significant difference between the results from the helium control and the carbon dioxide quencher.

Constant Pressure Quenching Experiment The IF(B,v'=0) to IF(X,v"=4) chemiluminescence produced a count of about 400 photons/sec at a pressure of 3.61 Torr prior to adding the quencher. CO_2 was added causing the total pressure to rise to 4.93 Torr and the count to drop to 190 photons/sec. The CO_2 was replaced by 0.07 Torr increments of helium. The photon count was recorded after each addition of helium both before and after adjusting the CO_2 flow so as to maintain the pressure constant (4.93 and 5.00 Torr). The emission intensity is plotted as a function of the percentage of CO in the combined helium and CO_2 flow.

The data is graphed in Figure (13) and does not show any statistically significant difference in the IF(B) emission intensity caused by reducing the percentage of CO_2 in the combined gases (helium and CO_2) from 100% to 30%.

From 30% to 0% [CO_2], there is a 17% rise in intensity. This slight difference may be attributed to flow tube reactor system instabilities and not caused by the effects of the [quencher/control]. Regardless of the cause, the slight variation does not suggest $O_2(b)$ has a dominant role in the IF-O_2* pumping reaction.

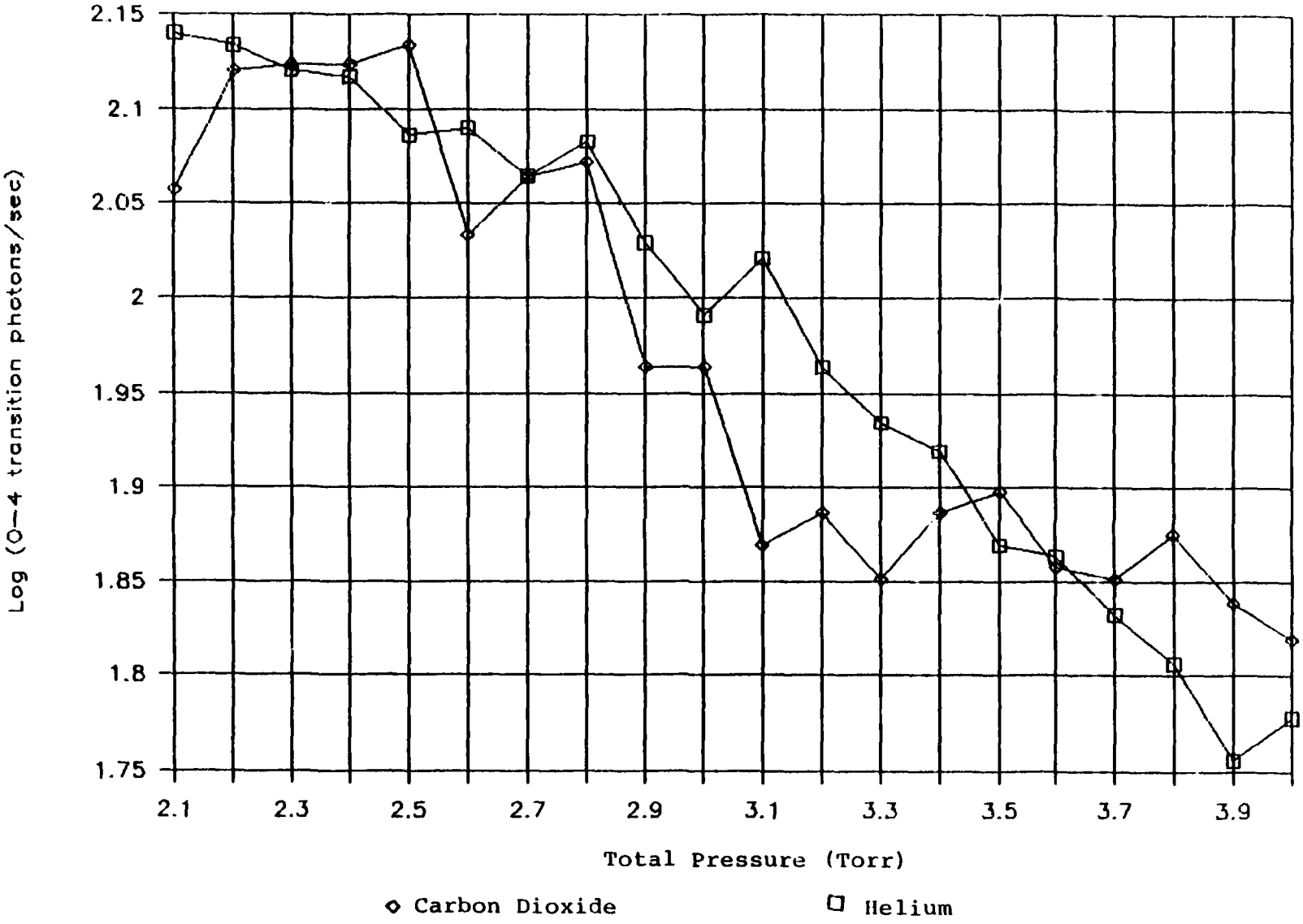

Figure 12. Relative Intensity of the IF(B,v'=0) to IF(X,v"=4) Transition as a Function of Total Pressure, Run #2

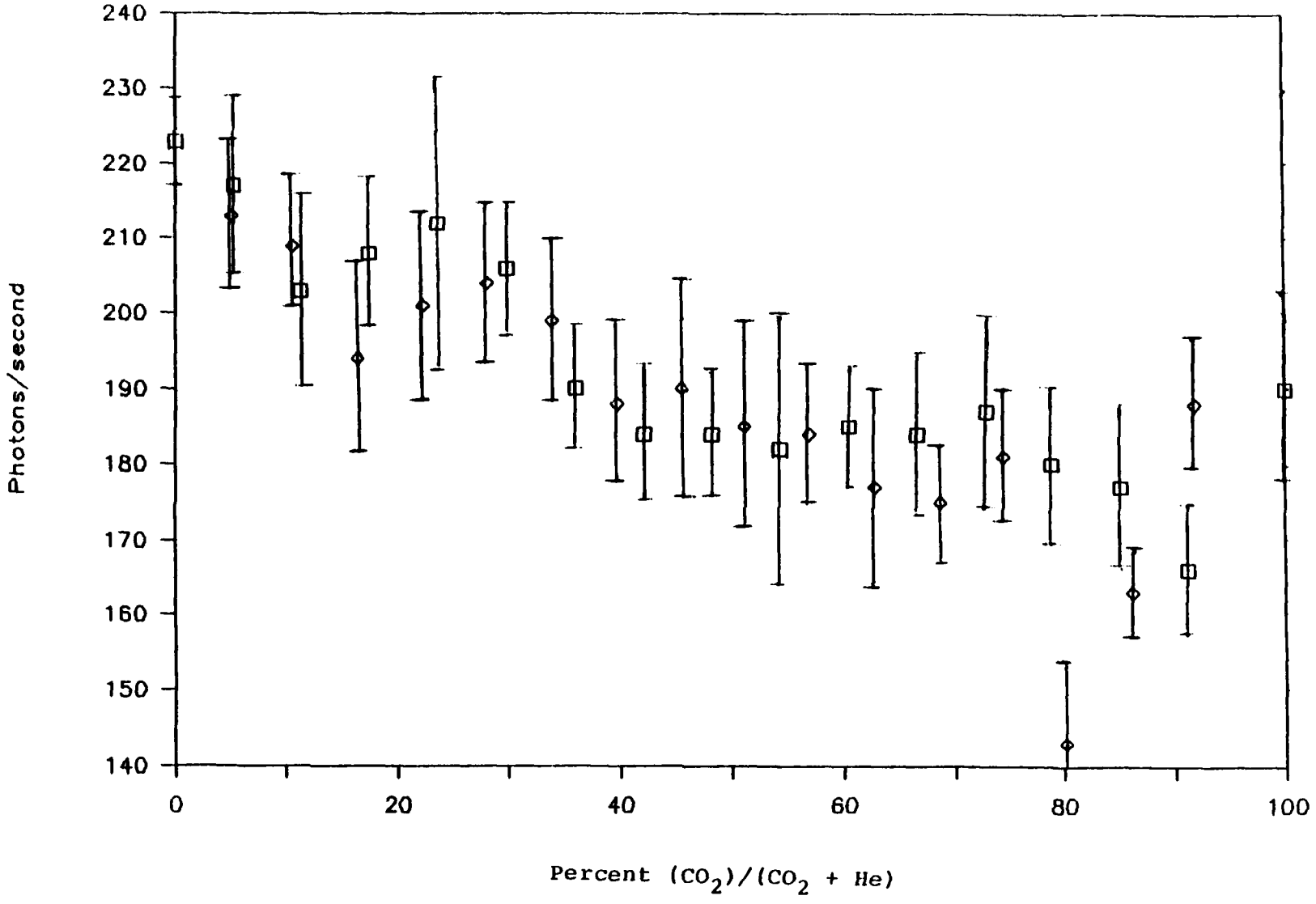

Figure 13. Relative Intensity of the IF(B,v'=0) to IF(X,v"=4) Transition as a Function of the Percent $(CO_2)/(CO_2 + He)$

VI. Conclusions

IF(B) chemiluminescence was generated from iodine monofluoride excited by singlet oxygen in a gas flow tube reactor. Spectral analysis of the chemiluminescence and quenching experiments were performed.

The IF(B) chemiluminescence spectral analysis clearly identified transitions originating from the IF(B,v'=0,1) energy levels. Weaker transitions originating from IF(B,v'=2) energy levels appeared to be present. There may also be some transitions originating from IF(B,v'=6) energy levels, but this is speculative due to the low intensity of the signal. Thus, all the primary transitions observed were from the lower vibrational levels of IF(B).

Data from the increasing pressure quenching experiments showed that there was no statistically significance difference between the effects the quencher (CO_2) and control (He) gases had on the IF($B \rightarrow X$) chemiluminescent intensity. The constant pressure quenching results only showed a slight increase in the intensity (17%) when the $O_2(b)$-quencher (CO_2) was totally replaced by helium. Thus, the quenching experiments' results suggest that $O_2(b)$ is not a primary energy transfer agent in the excitation of IF(X) for these experimental conditions.

In summary, the IF(B) chemiluminescence spectral analysis results are inconclusive in determining the role of

$O_2(b)$ in the IF(X $\rightarrow$B) excitation process. However, the quenching experiments' results suggest that $O_2(b)$ in not an important component. These findings argue against Model 1 presented in the theory section because it relies on $O_2(b)$ molecules. Models 2 and 3 require only $O_2(a)$ molecules. Additional experimentation is needed to assess the likelihood of Model 2 or 3 being the dominant mechanism.

VII. Recommendations

Vibrationally Excited IF(X).

Changing the IF(X) vibrational distribution should be done to differentiate between Model 1 and Model 2 presented in the theory section. This can be accomplished by delaying the time between formation of IF(X) and mixing it with excited oxygen. The diameter of the tube carrying the IF(X) generated from the CF_3I + F reaction can be increased to slow down the velocity and thereby allow the IF(X) to relax below the v"=6 levels prior to mixing with singlet oxygen. Increasing the diameter of the tube is suggested instead of changing the length to minimize the effects caused by dissociation of the IF(B) molecules due to wall collisions.

A study similar to this thesis should be performed using highly excited ground state IF(X). Vibrationally excited IF(X) should be prepared from F + I_2 which produces IF(X,v">10).

Improved Flow Metering.

Mass flow meters should be used to measure the actual instead of relative gas flow rates to allow determination of quenching coefficients. The metering should also be done as close as practical to the mixing region of the individual reactants to make the system more responsive and to reduce the likelihood of residual gases affecting measurements.

Controls.

Because the addition of gas to the system affects the flow and chemiluminescent flame dynamics, control gases should continue to be used for any quenching experiments.

Singlet Oxygen Production

Because the $[O_2(b)]$ may have been severely reduced due to wall collisions (16:41) before reaching the IF(X) molecules, the microwave cavity used to generate the O_2* should be moved as close as practical to the reaction chamber. Experiments should be done to determine if this increases the $[O_2(b)]$. If the concentration is indeed increased, additional experiments should be accomplished to determine its effect on IF(B) production.

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Thesis Chairman: Won B. Roh
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Abstract

Chemiluminescence was observed from Iodine Monofluoride (IF) excited by singlet oxygen in a gas flow tube reactor as a means to study the O_2-IF energy transfer mechanism. Although several researchers have demonstrated singlet oxygen's ability to efficiently pump IF(X) to the IF(B) state, the exact details of the processes have not been determined. The purpose of this research was to conduct IF(B) chemiluminescence spectral analysis and O_2(b)-quenching experiments to further define the excitation processes and to develop plausible mechanistic models based on experimental results. The spectral analysis revealed that the majority of the IF(B) to IF(X) transitions originated from the IF(B,v'=0) and IF(B,v'=1) vibrational energy levels. The O_2(b)-quencing experiments suggest that O_2(b) is not critical in the excitation of IF(X) under the conditions of this research. Two plausible mechanistic energy transfer models were presented based on experimental results.