



This is to certify that the
dissertation entitled

**MODELS FOR SIGNALS AND NOISE
IN LASER-INDUCED IONIZATION
SPECTROSCOPY**

presented by

Max F. Hineman

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Major professor

Date Dec. 7, 1987



RETURNING MATERIALS:

Place in book drop to
remove this checkout from
your record. FINES will
be charged if book is
returned after the date
stamped below.

--	--	--

MODELS FOR SIGNALS AND NOISE IN LASER-INDUCED IONIZATION
SPECTROSCOPY

by

Max F. Hineman

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1987

Abstract

Models for Signals and Noise in Laser-Induced Ionization Spectroscopy

by

Max F. Hineman

Laser-induced ionization (LII) techniques were recently developed as methods for the analysis of trace metals in flames. The LII techniques can be divided into two classes of experiments. In the first type of experiment a laser is used to induce a transition in an analyte atom. This increases the collisional ionization rate of the analyte. The increased ionization is detected as an increase in current collected by a set of biased probes. The second type of experiment uses a second photon, from the same or a second laser, to photoionize the excited analyte. The energies of the excited state of the analyte and the ionizing photon and the ionization energy of the analyte determines which of these two types of experiments is the most sensitive. The work presented here considers both types of experiments. In the experiments reported here pulsed lasers are used as sources of the excitation and ionization photons. Specifically, in these experiments a Nd:YAG pumped dye laser, with a frequency doubling option on the output of the dye laser, are used. Because the signals were fast pulses (200 ns) at low repetition rates (10 Hz), gated detection was necessary.

Two aspects of LII spectroscopy are explored in order

to examine the precision of the experiment and the accuracy of simple theoretical models. First, methods for maximizing the signal-to-noise ratio in LII experiments are presented. Models for the noise in LII signals are derived from simple signal models. The noise models are fit to experimental noise-versus-laser power data to obtain the values for the model parameters. The fitted models are then used to predict signal noise ratios for LII experiments.

Second, two theoretical models for the LII signal are compared, the density matrix formalism and the rate equations, which are a simplified form of the density matrix. The calculated ionization yields from the two models were compared to examine the accuracy of the rate equations model for laser pulses on the order of a few nanoseconds.

TABLE OF CONTENTS

Chapter		Page
	LIST OF TABLES	vi
	LIST OF FIGURES	vii
I	INTRODUCTION	1
	A. Overview of Laser-Induced Ionization	1
	B. Overview of Dissertation	2
	C. Historical	4
	1. Optogalvanic Spectroscopy in Discharges	5
	2. Resonance Ionization Spectroscopy (RIS) and Resonance-Enhanced Multiphoton Ionization (REMPI)	6
	3. Optogalvanic Spectroscopy in Flame Cells	9
II	Experimental	13
	A. Overview of the Experimental System	13
	B. The Laser System	15
	C. The Flame Systems	19
	D. Signal Collection, Amplification and Processing	24
	E. Absorbing Solutions	31
	F. Reagents	33
III	Modeling Signals, Background and Noise in Flame Laser Induced Ionization Experiments	34
	A. A Simple Model for Noise in LII Experiments	35
	1. Derivation of the Model	35
	2. Fitting the Data to Model Parameters	42
	3. Predictions of the Model	54
	B. An Extended Model	63
	1. Derivation of the Model	65
	a. Case a): Single Laser Resonance Enhanced Photoionization	65
	b. Case b): Two Laser Photoionization Experiments	66
	c. Case c): Collisional Ionization	66
	2. Fitting the Data to Model Parameters	67
	3. Predictions of the Model	68
	C. Flame Flicker	71
	D. Conclusions	75
	E. Appendix	77

IV	Comparison of Models for LII Signals	89
	A. The Density Matrix Formulation for Laser Excitation in Flames	90
	1. Single Mode Excitation	96
	2. Multimode Excitation	98
	B. The Rate Equations Approach	103
	C. Calculations of Parameters	107
	1. Collision Induced Rates	108
	2. Atom-Field Interactions	113
	3. Ion-Electron Recombination Rates	116
	4. Characteristics of Dye Lasers	119
	D. Results of Calculations	121
	1. The Negligibility of Recombination	124
	2. Highly Saturated Transitions	125
	3. Weak Transitions	132
	a. High Laser Powers	134
	b. Low Laser Powers	134
	4. Effect of Quenching Rates	137
	5. Effect of Dephasing Rates on the Density Matrix Model	139
	E. Conclusions	141
V	Summary and Future Directions	142
	A. Summary	142
	B. Future Directions	143
	References	147

LIST OF TABLES

Table	Page
3-1 Power Dependences and Coeffiecients	49
3-2 Parameters From Noise Fits	53
3-3 Comparison of Two Noise Models	70
3-4 Power Dependences at Various Wavelengths	87
4-1 Collisional Deexcitation Rate Constants	110
4-2 Off Diagonal Density Matrix Decay Rate Constants	112
4-3 Einstein Coefficients and Rabbi Frequencies	117
4-4 Dye Laser Characteristics	120
4-5 Parameters Used for Calculations	123

LIST OF FIGURES

Figure	Page
2-1 Simplified Schematic of the Experimental System	14
2-2 Time Resolved Electron Pulse	16
2-3 Laser System Diagram	17
2-4 Gas Flow Schematic	20
2-5 Premixed Burner Design	23
2-6 Diffusion Burner Design	25
2-7 Current Sensitive Preamplifier Design	27
2-8 Preamplifier Frequency Response	29
3-1 Atomic Level Scheme	36
3-2 Energy Levels for Mn and Na	43
3-3 Power Dependence of the Background Signal	47
3-4 Power Dependence of the Mn Signal	48
3-5 Fit of the Background Noise to the Model	51
3-6 Fit of the Total Noise in the Mn Signal	52
3-7 Predicted Signal to Noise Ratio	56
3-8 Effect of Background Sensitivity on S/N	58
3-9 Effect of Background Sensitivity on S/N	60
3-10 Effect of Signal Power Dependence on S/N	62
3-11 Effect of Laser Power RSD on S/N	64
3-12 Fit of the Extended Model to Noise	69
3-13 Effect of the Saturation Irradiance on S/N	72
3-14 Experimental System for Emission Measurements	76
3-15 Background Ionization Spectrum 280 nm	80

3-16	Background Ionization Spectrum Near the Mn Line in the H ₂ /O ₂ /Ar Flame	82
3-17	Background Ionization Spectrum Near the Mn Line in the C ₂ H ₂ /Air Flame	83
3-18	Background Ionization Spectrum Near the Na Line in the H ₂ /O ₂ /Ar Flame	84
3-19	Background Ionization Spectrum 420 nm	85
4-1	Transition Diagram for the Density Matrix Model	95
4-2	Transition Diagram for the Rate Equations	104
4-3	Comparison of Calculation Results for Single Mode Excitation	127
4-4	Error in Rate Model for Single Mode Excitation	128
4-5	Comparison of Calculation Results for Multimode Excitation	130
4-6	Error in Rate Model for Multimode Excitation	131
4-7	Error in Rate Model for Spectrally Narrowed Multimode Excitation	133
4-8	Error in Rate Model for Weak Transitions	135
4-9	Error in Rate Model for Weak Transitions, Spectrally Narrowed Excitation	136
4-10	Error in Rate Model for Weak Transitions, Low Laser Powers	138
4-11	Error in Rate Model for Highly Quenching Flames	140

Chapter I - Introduction

A. Overview of Laser-Induced Ionization Spectroscopic Methods

Irradiation of a sample reservoir with light of a wavelength corresponding to a resonant transition of the analyte contained therein increases the rate of ionization of the absorbing species. This increased ionization arises because the excited state analyte is more efficiently ionized than the ground state analyte. Ionization efficiency increases because the energy of the excited state is closer to the ionization energy. This has been called the optogalvanic effect (OGE) and was first observed by Foote and Mohler (1) in 1925. In 1928 Penning (2) measured the increase in current through a neon discharge when it was irradiated by another neon discharge. The application of this effect to analytical spectroscopy however, was not developed until 1976, after the introduction of tunable dye lasers. This new technique uses a flame as a cell for analyte atoms which are excited by a laser beam, and has been called laser-enhanced ionization (LEI) (3,4). The increased ionization of analyte atoms is detected by a set of biased probes placed in the flame close to the laser beam. In the ten years since its introduction, LEI has become one of the most sensitive methods available for trace metals analysis. The sensitivity of the LEI method results

from two of its properties, 1), the high collection efficiency (100%) for the ions formed and 2), the ability of high-powered, pulsed lasers to saturate resonant transitions resulting in high ionization efficiencies. A related technique has also been developed in which a second photon from the same, or a second laser can be used to photoionize the excited atom. This technique is called dual or direct laser ionization (DLI) (5). Whether LEI or DLI is most efficient for a particular case is a function of the energy difference between the pumped excited state and the ionization continuum (6). The method which gives the higher sensitivity reflects a trade-off between the efficiency and the sources of noise, which include the laser, the flame and the signal collection electronics. Throughout this dissertation, when both techniques are referred to indiscriminantly, the term laser-induced ionization (LII) will be used.

B. Overview of the Dissertation

This dissertation is comprised of six chapters. Chapter I serves to introduce the techniques of laser-induced ionization spectroscopic methods and briefly discuss their histories and applications. First the techniques are introduced and then a brief history is presented.

Chapter II discusses the experimental apparatus used in the work being presented in Chapter V. The apparatus is

broken down into its components which are described separately. First, the laser system is described. The flame and burner systems are then discussed with attention paid to the reasons behind various design features. The signal collection is discussed in the next section. The amplifier designed for these experiments is described and its characteristics presented. Once again attention is paid to the reasons for its various attributes. Signal processing equipment used to enhance the signal-to-noise ratio of the ion current is then described. The last sections of Chapter II describe the method of laser attenuation and the reagents used in these experiments.

Chapter III discusses a practical experimental problem, noise. Specifically, the effect of various experimental parameters on the background level and the magnitude of the noise is examined. A model for noise in an LII experiment is derived from a simplified signal model. The resulting equations are fit to experimental data, by means of a Simplex algorithm to determine the optimum parameters for the system. These parameters are then used to make predictions about the effects of experimental parameters on the signal-to-noise ratio for LII experiments.

Chapter IV discusses the various models used to describe the laser-induced ionization of atoms. These include the density matrix and the rate equation approaches to the problem. The equations to describe the signal obtained are derived and some simplifying assumptions are

made. The equations are then used to elucidate the effect that various assumptions in the derivations of the equations and various experimental parameters have on the predictions of the models. The validity of the rate equations under various conditions is evaluated.

The final chapter summarizes the work presented and presents some possible future directions for this work.

C. Historical

Since the introduction of the optogalvanic effect with laser sources in 1976 (3,4), ionization-based detection schemes have been used in many areas of spectroscopy. Applications have been reported in the areas of analytical spectroscopy - for determinations of trace amounts of elements and molecules, diagnostic studies of flames and plasmas, and determination of the absorption spectra of atoms and molecules. This review will break the area into the following groups separated essentially by sample cell type; 1), optogalvanic spectroscopy in discharges; 2), resonance ionization spectroscopy and resonance-enhanced multiphoton spectroscopy, techniques for detection and spectral observations of atoms and molecules in vacuum chambers and other inert media, 3) laser-induced ionization spectroscopic methods in flame cells. The term inert media is used here to denote environments which are not highly

reactive or characterized by large collision rates and energetic collisions.

1. Optogalvanic Spectroscopy in Discharges

One of the two papers which reintroduced the OGE (4) describes its use to detect species contained in a discharge tube. The work of Foote and Mohler and that of Penning was performed in discharges. The OGE has been used to detect both atoms (7,8,9) and molecules (10,11) in discharges. Stepwise excitation has been implemented to increase the sensitivity of the technique (12,13). Stepwise excitation involves the use of two tunable lasers operating at two resonances of the analyte which share a common intermediate state. The first laser promotes the atom to an excited state and the second promotes the excited atom into a higher-energy excited state. In this way the energy required for ionization is reduced even more than in a single-excitation experiment and the collisional ionization rate and, therefore, the sensitivity of the experiment increases. The OGE has also been used to frequency lock CO₂ and tunable diode lasers (14,15,16) and for wavelength calibration of tunable dye lasers (17,18). These calibrations or locks are made by passing the laser beam, or a portion of the beam, through a cell or discharge containing a species whose transition wavelengths are well known; the OGE signal produced is observed. The OGE has

been used to study Rydberg transitions in atoms (19,20,21) and rovibronic levels in molecules, even though the increase in ionization rate for these transitions is not as large as for transitions in the visible and ultraviolet regions of the electromagnetic spectrum.

There have been many studies attempting to ascertain the mechanisms for ionization in optogalvanic spectroscopy. Dreze et al. (23) have shown that direct collisional ionization is not the predominant mechanism for ionization in hollow cathode discharges, but instead much of the energy from excitation of the analyte is redistributed through collisions. The mechanisms of the OGE in various plasmas have been studied by several workers (24,25,26) as well as Penning ionization in hollow cathode plasmas (27).

Carlson and coworkers have studied the optogalvanic spectrum of TiO in a hollow cathode discharge, and Engleman et al. (29) have examined the effect of optical saturation of hyperfine intensities in the OGE spectrum of Lu. The OGE spectrum of SiH has been observed in a glow discharge (46) and some transitions of HCO have been observed in an rf discharge (30).

2. Resonance Ionization Spectroscopy (RIS) and Resonance Enhanced Multiphoton Ionization (REMPI)

RIS is a multiphoton ionization spectroscopic method in which at least one transition to a real excited state is resonant with the laser frequency or a multiple of the laser

frequency. The resonance increases the sensitivity of the multiphoton ionization technique. In fact, RIS has achieved single atom detection. The sample cell for RIS is usually a proportional counter, a vacuum chamber or the ionization region of a mass spectrometer. This section will also discuss experiments employing other non-reactive gas cells. Hurst et. al. (31) reviewed the RIS technique in 1979. This extensive review has a table of ionization schemes for almost every element in the periodic table. It also developed theoretical models for the ionization process and presented methods for constructing many experiments including those for absolute measurements of photoionization cross sections, atomic excited state densities and fission fragment detection. More recently Donahue and Young (32) have reviewed RIS with mass spectrometric detection.

Hess and Harrison (33) have performed RIS in a glow discharge with mass spectrometric detection for the analysis of solid samples. RIS has also been coupled with different atomization sources such as filaments, (34-36,39) atomic beams (37,41) and ion beam sputtering (38) for the analysis of solid samples. RIS has been used for spectroscopic studies of autoionizing states (40), electronic state distributions (38), the effects of gas phase collisions (43,44) and Doppler free spectra (41). In one study lasers were used to enhance the efficiency of electron impact ionization for Ba atoms (41). Multiple resonance schemes have also been used to increase the efficiency of the

ionization process (36,42). This requires the use of multiple tunable lasers and so it is more experimentally complex than schemes involving only one resonance excitation step.

When molecular species are being observed the term resonance-enhanced multiphoton ionization (REMPI) is commonly used. Parker (43) has recently reviewed this technique. Usually, small molecules for which the rotational structure can be resolved have been studied. For example, NO has been extensively studied. Cool (47) made quantitative measurements of NO density in a gas cell using a 2+1 REMPI scheme. The 2+1 notation means that two photons were absorbed to reach an excited state and one more was absorbed for ionization. Jacobs et.al. (48,49) have formulated a method for reducing 1+1 REMPI spectra to ground electronic state population distributions. Rottke and Zacharias (50) populated single rotational levels of excited electronic states of NO and then measured the lifetime of these levels by time-delaying the ionizing laser beam. Double resonance spectroscopy has also been performed with ionization detection in a 2+1+1 scheme (53). Radical species have also been studied. For example, a 2+1 scheme was used to observe HCO formed by photolysis of acetaldehyde in a vacuum chamber (51). Microwave interferometry has been used to measure electron densities after REMPI and these densities were used to calculate photoionization cross sections (52).

Larger molecules have also been studied with REMPI. For example, argon-benzene van der Waals complexes formed in supersonic beams have been studied (54). Towrie et al. (55) used REMPI to identify and quantitate an impurity in the filler gas in their proportional counter which gave rise to background interferences. Many different aromatic compounds have been studied by REMPI in supersonic jet expansions with mass spectrometric detection (56-63). Pulsed laser desorption has also been used to volatilize involatile compounds prior to supersonic beam REMPI (64). The use of supersonic expansions has become popular because it simplifies the spectra by concentrating the molecules in low rotational energy levels of the ground electronic state. This "cooling" of the molecules is desirable because large molecules have closely spaced rotational levels which will not be resolved using conventional ultraviolet or visible lasers. The rotational cooling will therefore narrow the vibrational bands observed, making it possible to identify isomers and other molecules with overlapping spectra.

3. Optogalvanic Spectroscopic Methods in Flame Cells

The first observation of the optogalvanic effect in a flame was made in 1976 (3). The laser was directed into the flame and its wavelength was tuned to match a resonant transition of the Na which had been introduced by means of a nebulizer. The excitation of the Na increased the

ionization rate and this increase was detected by a set of biased probes placed near the laser beam's path through the flame. The name laser-enhanced ionization was given to the technique. In this first study a CW dye laser was chopped and lock-in detection was used. The next study in the area used a flashlamp-pumped dye laser to achieve saturation of larger flame volumes and showed that low detection limits could be achieved if the energy difference between the pumped excited state of the analyte and its ionization threshold was small (65). Then a frequency doubler was added after the dye laser to allow the use of transitions in the ultraviolet (66), which allowed more elements, with higher ionization energies, to be ionized efficiently. This paper also developed the theory of LEI signals more completely by using a rate equations approach to the atomic systems studied. In another study (67), an equation for a sensitivity factor based on experimental parameters was developed.

Many studies of interferences in LII in flames have been published (68-73,77). In 1979, two groups published papers which showed the use of stepwise excitation to improve the sensitivity of LEI experiments for higher ionization energy elements (74,75).

In 1981, optogalvanic spectroscopy using photoionization of the excited atom instead of collisional ionization was introduced by van Dijk et al. (76). This technique was termed dual laser ionization (DLI). In some

cases, depending on the excited state-to-ionization threshold energy gap, photoionization was shown to be a more sensitive method for optogalvanic studies. Ion collection for LII experiments has been studied extensively.

Schenck and coworkers (77) did a thorough study of ion collection for ions produced by LII in flames. Berthoud et al. (78) have examined the effect of probe voltage and position on the electron pulse shape in LII signals. It should be clarified that the electrons move much more quickly than the ions and therefore the electron pulse is separated from the ion pulse temporally. The electron pulse, because it is much quicker and therefore exhibits a higher peak current, is more useful for analytical measurements. Lin et al. (79) used ion mobility measurements to calculate flame temperature.

LII has been used to detect molecules in flames (80-83), showing that it is a useful tool for combustion diagnostics. LII has also been used to examine atomic hydrogen and oxygen in flames (84,85), both of which are very important in primary combustion reactions. More recently LEI has been used to determine the lifetime of metastable Tl and Pb levels in air-acetylene flames (86) by varying the time delay between the first and second lasers in a two-step, stepwise LEI experiment. A nitrous oxide-acetylene flame was used to perform LEI experiments for the determination of refractory elements (87).

An inductively-coupled plasma has also been used as a source of atomic vapor but the probes were found to be very susceptible to picking up rf interference from the plasma source (88). LEI experiments have also been performed in a graphite furnace atomizer (89). Stark structure has been observed in the Rydberg levels of Li using LEI spectroscopy, and it has been used to study the electric field in the flame created by the biased probes used to collect the ions (90). Turk and coworkers (91) have taken three dimensional LEI spectra by scanning both laser wavelengths in a two-step, stepwise LEI experiment. The ionization yield for Li in an LII experiment has been measured by Smith et al. (92) by combining absorption and ionization measurements to obtain both ground state density and laser-induced ionization measurements. Fluorescence of Sr^+ ions has been used to monitor the time decay for these ions created in LII experiments in flames (94). One criticism of many dye-laser-based spectroscopic techniques used for chemical analysis is that, in order to cover a useful spectral range, dyes must be changed many times making the analysis more complex and take longer. Axner and coworkers (93) have investigated the multielement capabilities of LEI in flames by observing the number of elements which could be detected within the tuning range of a single laser dye and the sensitivity for each element.

Chapter II - Experimental

One of the advantages of the ionization techniques used in flames is the simplicity of the ion detection system. Biased probes in electrical contact with the flame can detect all of the ions formed using fields of less than 1000 V/cm. This chapter will discuss the apparatus used to form and detect ions in the experiments described in Chapter III.

A. Overview of the Experimental System

The experimental system used for the studies described in this dissertation is pictured in Figure 2-1. A Meker burner flame cell is used for the formation of free metal atoms. Two types of burners are used for these studies. One is a premixed air-acetylene burner. The other is a laminar-flow diffusion burner. Analyte was introduced into the flame by using either a crossed-flow pneumatic nebulizer (with the premix burner) or a concentric-flow pneumatic nebulizer (with the diffusion burner).

A neodymium yttrium aluminum garnet (Nd:YAG) laser-pumped dye laser was used to generate tunable radiation. A frequency-doubling crystal was used when ultraviolet radiation was necessary. A water-cooled, stainless steel electrode was biased negatively and immersed in the flame. The burner head itself was used as the anode to complete the

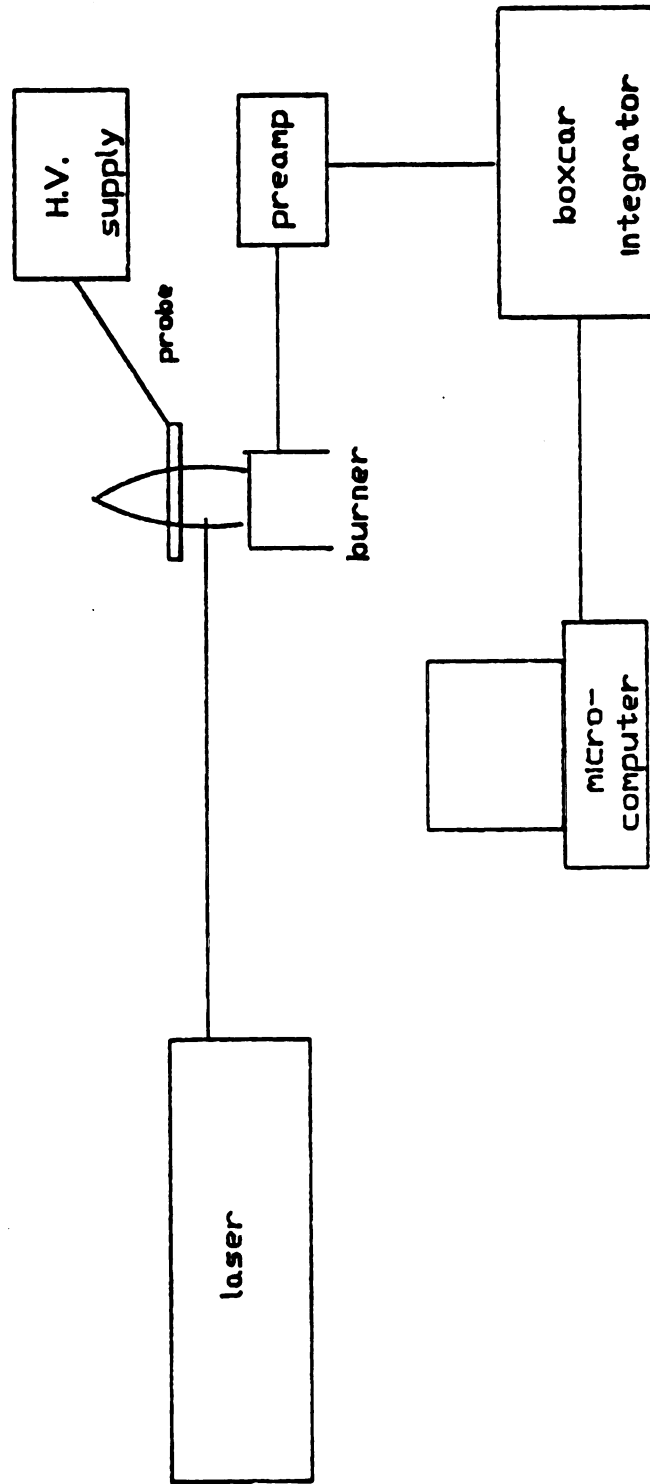


Figure 2 - 1 Simplified Experimental System Description

probe pair. The ions and electrons formed in the flame migrate to the probes under the influence of the electric field and are collected. The resulting current pulse is amplified by a fast current-to-voltage converter with gain. The electron transit times for this configuration are on the order of 100 ns and the laser fires with a repetition rate of 10 Hz. The low duty cycle of the signal requires the use of a gated integrator to improve the signal-to-noise ratio of the experiment. The output of the gated integrator is taken to a computer interface for data conversion and storage on a microcomputer. A typical time-resolved electron signal is shown in Figure 2-2.

B. The Laser System

The laser system is pictured in Figure 2-3. The Nd:YAG laser (model DCR-2A, Quanta-Ray, Mountain View, CA) was used to pump the dye laser and also as a source of fixed wavelength radiation. The Nd:YAG rod is pumped by high power pulsed flashlamps. Only the second (532 nm) or third (355 nm) harmonics of the Nd:YAG radiation (1064 nm) were used for pumping the dye or for fixed wavelength radiation. The harmonics were generated in a commercial harmonic generator (HG-2, Quanta-Ray, Mountain View, CA) with a thermostated housing, which increased the long term power stability of the harmonics. The maximum power available in the second harmonic was approximately 30 MW at the peak and

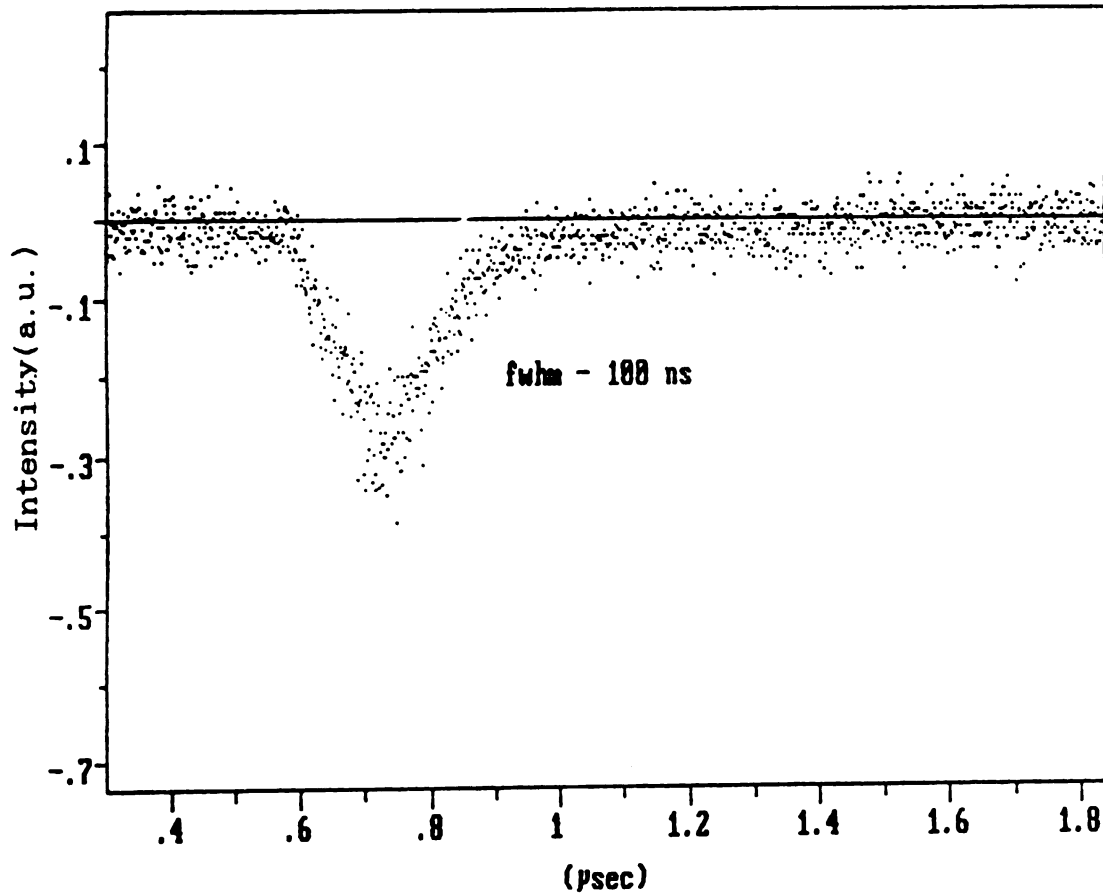


Figure 2 - 2 Time-Resolved Electron Pulse Output from the Preamplifier

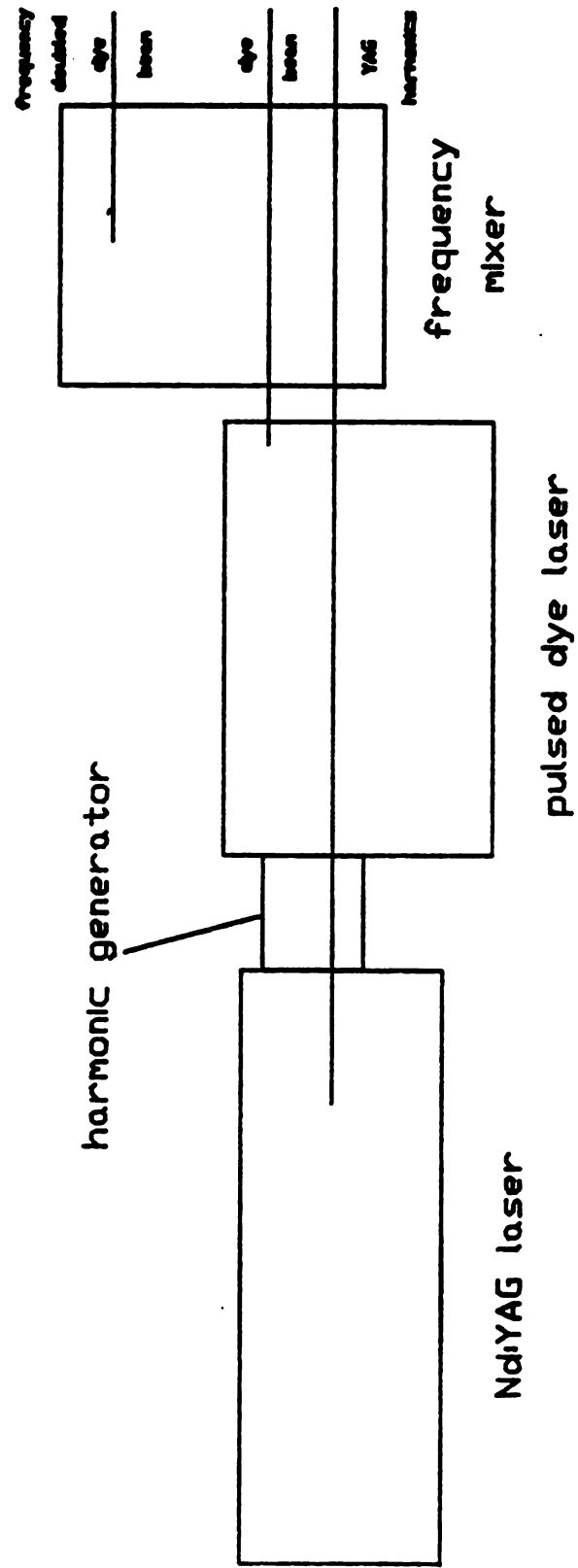


Figure 2 - 3 Nd:YAG Pumped Dye Laser with Frequency Mixing

could be adjusted by varying the energy per pulse applied to the flashlamps. The third harmonic had a maximum output power of approximately 10 MW. The dye laser is also a commercial system (PDL-1 or PDL-2, Quanta-Ray, Mountain View, CA) which consisted of an oscillator and two amplifier sections. One of these was optional and used only with blue (emission wavelength) dyes because of their lower output power to input power efficiencies.

For the generation of tunable ultraviolet radiation the output of the dye laser was directed into a commercial frequency doubler and mixer (WEX-1, Quanta-Ray, Mountain View, CA). The wave mixer had available crystals to either frequency double the dye laser radiation or sum the dye and the Nd:YAG fundamental (1064 nm) frequencies. The crystals are angle tuned to attain the index matching condition necessary for efficient mixing. The mixing unit is equipped with an automatic tracking mechanism which angle tunes the crystal to maintain maximum conversion efficiency as the dye laser is wavelength scanned. The laser pulse power could be adjusted by varying the energy per pulse applied to the flashlamps which pumped the Nd:YAG rods or by using neutral density filters or absorbing solutions after the beam had already been generated. The reasons for using one or the other of these methods will be discussed later.

The appropriate output beam from the laser system was directed onto another table, which supported the flame system and detection electronics, with a quartz prism and a

UV-enhanced aluminum mirror. Scanning of the dye laser wavelength was performed using a computer-controlled stepper motor drive built and programmed by Ralph Thiim (120). It consisted of a microcomputer designed by Bruce Newcome (119) which was triggered by a pulse sent by the gated integrators computer interface and stepper motor controller drive. The program allowed scanning between two different wavelengths at a speed set by the trigger rate or slewing to any desired wavelength.

C. The Flame Systems

There are two different flame systems used for this work. The first is a premixed laminar-flow air-acetylene burner which was built in the departmental machine shop. The second is a laminar-flow diffusion burner which was built after a design by Krupa et al. (97). The major difference between the two types of burners is that in the premixed flame the fuel and oxidant flows are mixed prior to exiting the burner, whereas, in the diffusion burner the fuel and oxidant flows do not mix until after they exit the burner. Each is described separately below.

The gas flows for both burners were controlled by dual stage regulators at the tanks followed by precision flow meters (series FM-1050, Matheson Instruments, Horsham, PA). Figure 2-4 diagrams the gas flow paths for both burners.

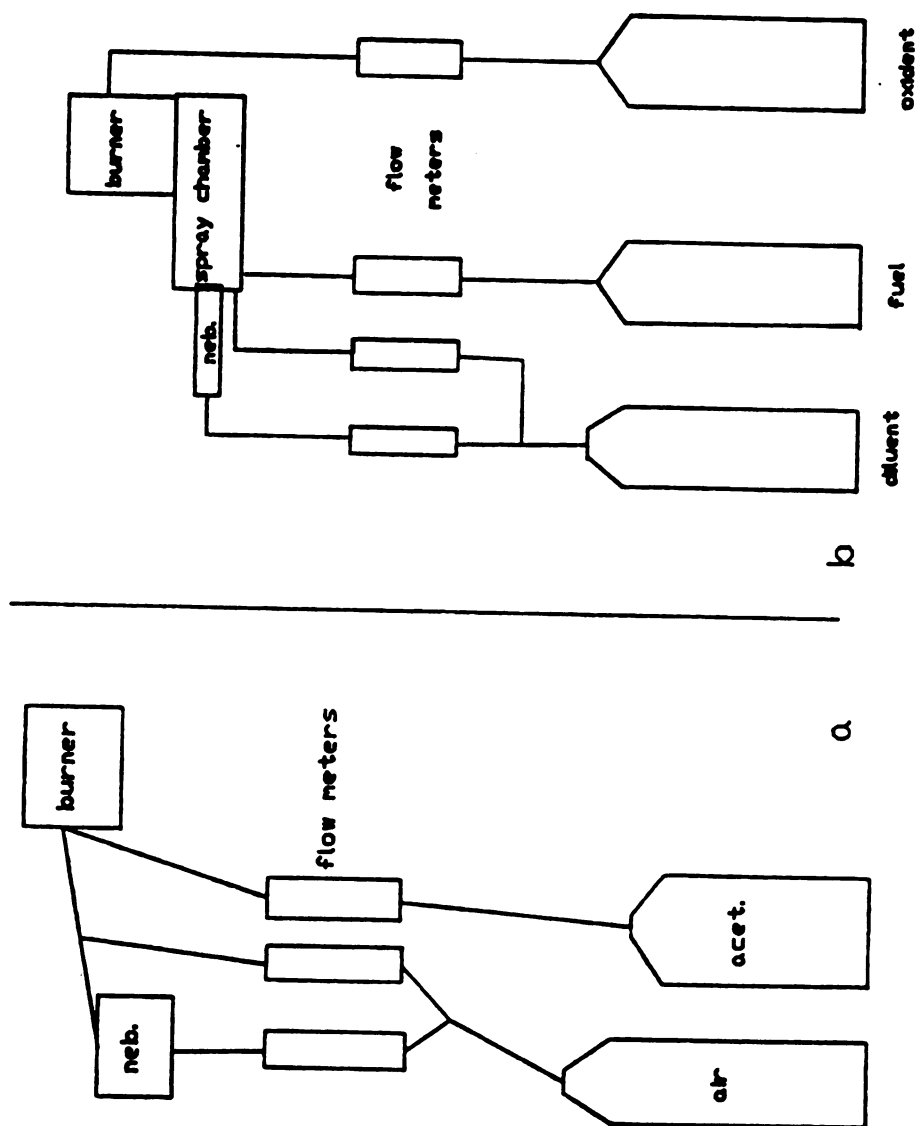


Figure 2 - 4 Gas Flow Map for: a - the diffusion burner, b - the premixed burner

1. Premixed Burner

There are certain criteria that must be considered when designing a premixed flame burner. The flow velocity of the unburnt flame gases must approximately match the burn velocity of the gas mixture. When the burn velocity exceeds the flow rate, the exit holes must be small enough to quench the flame as it tries to burn back into the burner. This also suggests that the holes must be sufficiently long to allow this quenching to occur. The burn velocity of a stoichiometric air-acetylene mixture is 160 cm s^{-1} (95). Holes of 0.8 mm diameter or less have been shown to quench the air-acetylene flame regardless of flow rate (96).

Figure 2-5 is a diagram of the premix burner designed for these studies. The top is a 1 cm thick piece of brass with a 6 by 6 array of 0.8 mm diameter holes drilled through it. This is silver-soldered to a cylindrical body where the flame gases enter and mix. This design was optimized for total gas flow rates of approximately 3 L min^{-1} . This low flow rate minimized the amount of air in the auxiliary flow and also the number of times that tanks had to be changed. The use of flow rates up to 10 L min^{-1} did not create noticeably non-laminar flows or cause the flame to lift off the burner. The column in the center of the burner body aids the mixing of the air-acetylene mixture as it enters the burner. The blow-off cap on the bottom acts as a

pressure release in the unlikely event of a flashback and was incorporated as a safety feature.

This premixed burner required the use of an external nebulizer for sample introduction. A crossed flow nebulizer with air as the nebulizing gas was used for this application. The design of this nebulizer has been discussed by Curran (100) and will not be repeated here.

2. Diffusion Burner

The other burner used in these studies is a laminar-flow, diffusion burner based on the design of Krupa et al. (97). Figure 2-6 diagrams this burner head. The diagramed piece slides into a commercial spray chamber. The nebulizer gas is the diluent for the flame and it and the fuel mix in the spray chamber and enter the burner head from the bottom. They are carried to the top of the burner by the stainless steel capillaries. The oxidant enters the top chamber of the burner and exits through an array of holes in the top. The fuel/nebulizer gas capillary holes are larger to prevent clogging due to the sample mist. A water jacket was added around the top of the burner to cool the burner during operation.

The logic behind the design used is explored in the previously referenced paper (97), but a few of the reasons most important to this work will be reviewed here. This diffusion burner design allows many different fuel and

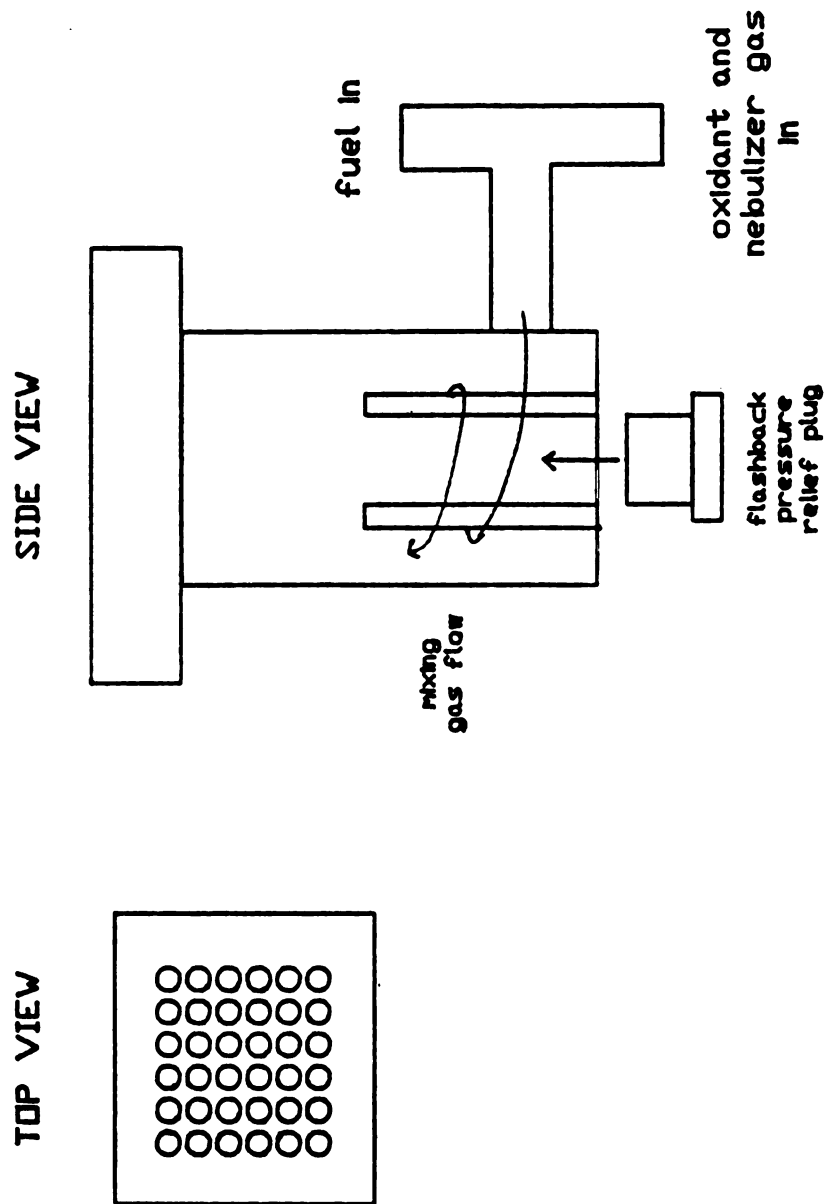


Figure 2 - 5 Premixed C_2H_2 /air Burner Design

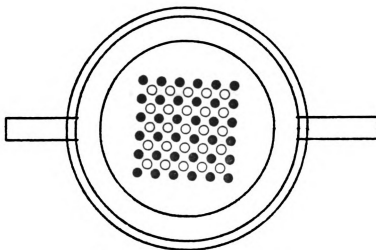
oxidant mixtures to be used because the gases, not having mixed until they exit the burner, cannot flash back. In these experiments a hydrogen-oxygen flame was diluted with argon. To do this in a premixed burner requires great care in the design and operation of the burner. The design used also allows the temperature of the flame to be varied, without varying the stoichiometry, by increasing or decreasing the diluent flow rate. Doing this in a premix flame requires great caution because the total flow rate and the burn velocity of the mixture are critical and both vary with the diluent level.

The maximum temperature that can be obtained is determined by the fuel and oxidant flow rates and the minimum diluent flow rate necessary to maintain stable nebulization of the sample. For this reason, fairly high flow rates were chosen for the hydrogen (~ 12 L/min) and oxygen (~ 6 L/min) so that a high temperature (> 2500 K) could be maintained, while using the nebulizer with flowing argon (~ 3 L/min) (97).

D. Signal Collection, Amplification and Processing

Signals were collected in the same manner for both burner systems and so this section does not treat them separately. The collection probe configuration used is the same as that used by workers at the National Bureau of Standards. A water-cooled stainless steel tube is immersed

Top View



● OXIDANT HOLES (0.031" dia.)

○ FUEL CAPILLARIES (0.042" i.d., 0.058" o.d.)

cooling water



cooling water

oxidant

Side View

1 cm.

fuel and diluent

Figure 2 - 6

Diffusion Burner Design

in the flame and biased negatively, usually to -1200 V relative to ground. The burner head itself is used as the anode and is connected to the input of a current-sensitive preamplifier which is discussed later. The burner is therefore connected through a $100\ \Omega$ resistor to ground. The laser beam and probe are parallel so that all ions formed in the flame along the path of the laser can be detected.

The preamplifier design was settled on after many trials and some discussion with Martin Rabb, the departmental electronics design specialist. The final design is shown in Figure 2-7. The design was based on the specific type of signal to be detected, a fast current pulse (see Figure 2-2) on top of a d.c. flame current. The current input from the burner passes across a $100\ \text{ohm}$ resistor to ground to obtain a voltage which is passed through a high pass filter to remove any d.c. components. This is connected to the non-inverting input of an operational amplifier configured as a voltage follower with a gain of 100. The output of this first stage is available as the final amplified signal or is the input to a second voltage follower with a gain of 10. This allowed two different gain outputs from the same amplifier without the introduction of switches to switch feedback resistors in the stages. Switches have stray capacitances which affect the response time of the amplifier and they tend to pick up radio-frequency interference (rfi).

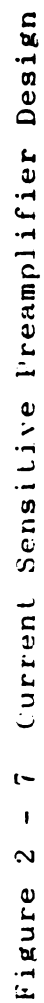


Figure 2 - 7 Current Sensitive Preamplifier Design

The amplifier circuit is housed in a shielded, grounded aluminum case to minimize rfi pickup. The operational amplifier used in both stages is an 'ultra fast' JFET amplifier (LH0032CG, National Semiconductor, Santa Clara, CA). It has a slew rate of 500 V/ μ s and an open loop bandwidth of 70 MHz. It was necessary to change to a two-stage amplifier with small gains in each stage from the previous single-stage design (100) because the electron signals which are being generated in this study are much faster than the ion signals being studied previously and the bandwidth of the amplifier drops significantly with gain (98,99). The frequency response characteristics of this amplifier are shown in Figure 2-8. The supply voltage (± 15 V) was taken from a commercial power supply (AD902, Analog Devices, Norwood, MA) in a homemade circuit placed in a shielded case.

The output of the preamplifier was connected to the input of a gated integrator (SRS 250, Stanford Research Systems, Palo Alto, CA) across a 1 k Ω load. This resistance was used because it did not noticeably load the amplifier and did not cause any impedance matching problems. The gated integrator was triggered using a variable output from the laser. This output could be varied from 500 ns before to 800 ns after the Q-switch of the laser opened. Thus, it was possible to trigger the boxcar before the laser pulse and therefore capture the entire electron pulse. The gate width of the gated integrator is continuously variable from

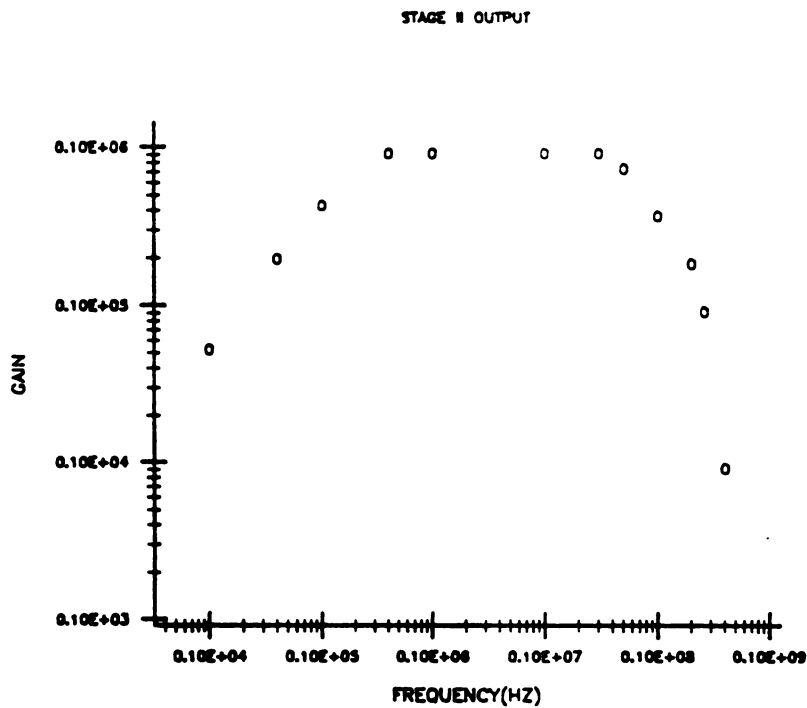
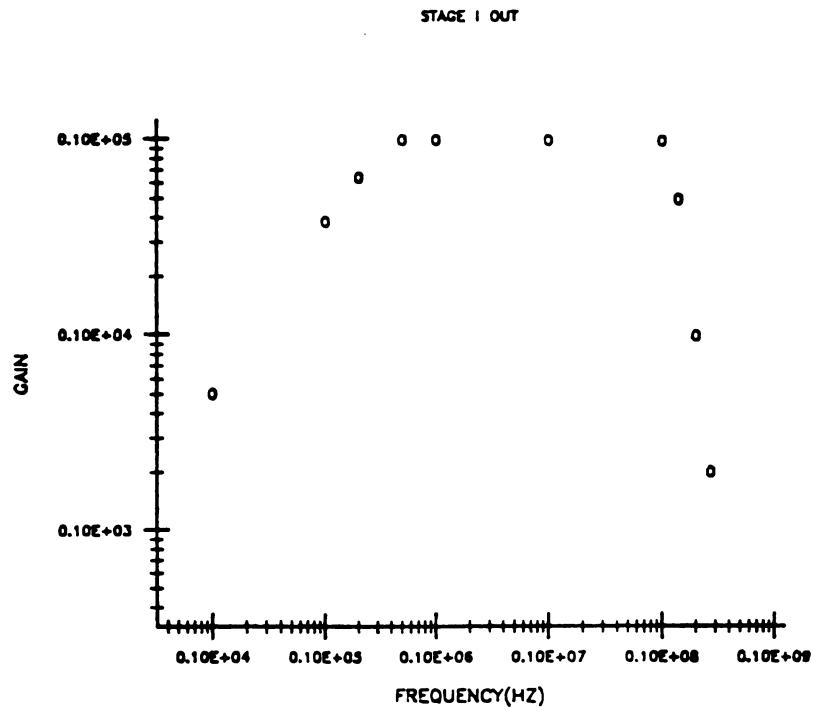


Figure 2 - 8 Preamplifier Frequency Response

2 ns to 15 μ s. For experiments where no time scanning was done the gate was held at 250 ns. This is slightly higher than the gate width for optimum signal-to-noise ratio improvement (101), but it allowed the integration of the entire electron pulse. Most of these experiments were done without averaging the data so that each data point represents the ions formed from one pulse of the laser. However, spectral scans were taken using a 10 point moving exponential average available on the front panel of the gated integrator.

The output of the gated integrator was connected to a commercial computer interface (SR245, Stanford Research Systems, Palo Alto, CA). This interface did analog-to-digital conversion and shipped the data to the microcomputer for storage and display. The interface also controlled gate scanning for time resolved data and supplied a trigger to the microcomputer which scanned the dye laser for spectral scans. This triggering scheme allowed spectra to be taken automatically with the wavelength known to within the precision of the counter on the dye laser.

The average power of the laser was measured with a commercial power meter (model 365, Scientech, Boulder, CO) with an absorbing disc calorimeter detector head (model 38-0101, Scientech, Boulder, CO). For measurement of the relative power of individual pulses, a fast PIN photodiode (model 4220, Hewlett Packard, Palo Alto, CA) was used. The photodiode circuit has been described previously (100). The

output of the photodiode circuit was taken into another gated integrator for ratioing with the ion signal or other signal processing. The gate width used for the photodiode output was 15 nanoseconds. This allowed for jitter in the time between the Q-switch synchronizing output and the light pulse output and prevented the photodiode pulse from moving out of the gate window.

All data processing, such as scale expansions, ratioing of signal to laser power, averaging and calculation of the standard deviation of a data set, was done with the commercial software provided with the gated integrator and computer interface (SR265, Stanford Research Systems, Palo Alto, CA). Fitting of the collected data to models was done using a SIMPLEX program supplied by Peter Wentzell (102), and run on a PDP 11/23 minicomputer (Digital Electronics Corp., Maynard, MA). The SIMPLEX method will be briefly explained in chapter III.

E. Absorbing Solutions

As mentioned previously there are two methods available for attenuation of the laser power for power dependence studies or for fixed power studies at lower powers. Either the energy per pulse applied to the flashlamps can be adjusted or the power of the beam can be attenuated after the laser. The first case is not the optimum choice for several reasons having to do with the operation of the

laser. The laser was designed with high powers in mind so that the pulse-to-pulse power variations are lowest at highest powers. The beam quality (divergence) is also better at the highest power. Changing the power applied to the flashlamps changes the power in the beam and therefore the absorptive heating in all of the crystals (lasing and non-linear) in the laser system. Therefore, the crystals must be allowed to re-equilibrate after each adjustment if power drift and beam shape changes are to be avoided. Also, the output power does not vary linearly with the energy input to the flashlamps; and therefore, it is difficult to predict the power change for a given increment of the flashlamp energy. For these reasons the power was varied using absorbing solutions in a quartz cell just in front of the flame. The choice of solutions was made due to a lack of available high-damage-threshold ultraviolet neutral density filter sets.

The absorber chosen was dichromate. It has several desirable qualities. It is a liquid absorbance standard in the region from 200 to 400 nm so its absorbance throughout this region is well documented (103). The photochemical stability of the solution is very high, and the temperature coefficient for absorption is very small so that the effect of prolonged exposure to laser radiation is not significant. A pH of 2.7 was set in the solutions by adding sulfuric acid. This pH was chosen because the dichromate is most stable in a pH range near, but not exceeding pH 3 (103).

Attenuation of the laser beam was achieved by consecutive 10 to 20 μ L additions of 1 mM potassium dichromate to a cell containing a sulfuric acid solution at pH 2.7. Laser power was measured after the attenuation and dc absorption measurements were made of the solution on a Hitachi spectrometer at the laser wavelengths used and the results were compared.

F. Reagents

All solutions were prepared with reagent grade chemicals. Sodium was obtained from sodium chloride (Fisher Scientific Co., Fairlawn, NJ). Manganese was obtained from manganous sulfate monohydrate (J. T. Baker, Phillipsburg, NJ). Dichromate for the absorbing solutions was obtained from potassium dichromate (Fisher Scientific Co., Fairlawn, NJ).

Chapter III

Modeling Signals Background and Noise in Flame Laser Induced Ionization Experiments

There are many sources of noise in a LII experiment. There are fundamental sources of noise, such as shot noise in the signal, background and d.c. flame current and Johnson noise in the resistors and the signal processing equipment. There are also other sources of noise. Flame flicker changes the concentration of absorbers along with collision rates, nebulizer fluctuations change the analyte concentration and laser power fluctuations change the extent of ionization for a given concentration of absorber. There is noise in the amplifier and other electrical circuits as well as radio frequency interference (rfi) pickup by the probes that add to the noise in the zero measurement. In most experiments it is desirable to optimize the precision, by maximizing the signal-to-noise ratio of the experiment. The selection of optimum conditions for atomic emission, absorption and fluorescence in the gas phase has been discussed by many authors (121-124). This topic has not yet been discussed for LII spectroscopy in flames.

In this chapter, the expressions for noise in an LII experiment are developed from simple models for the signal and background. The data from power dependence experiments are used to fit the model parameters. The models and the

parameters of the fit are used to examine the effect of various experimental parameters on the LII signal-to-noise ratios and to predict the optimum laser power for maximum signal-to-noise ratio. In the next section a more general noise model is developed and fit in the same manner. In the final section of the chapter, the measurement of the flame flicker noise value is discussed.

A. A Simple Model for Noise in LII Experiments

1. Derivation of the Model

The first model which will be derived for noise in LII experiments will use a simple equation for the signal. This is a simplified version of the rate equation model described in chapter 4. The model for the signal will be based on a two bound-level atom with an ionization continuum (see Figure 3-1). The solution to the simplified form of the rate equations has been derived by Curran (100). The symbols and rate processes are described below. In Figure 3-1, n_1 , n_2 , and n_i are the population densities of the three levels (cm^{-3}), E_d is the spectral irradiance of the exciting dye laser ($\text{W cm}^{-2} \text{ Hz}^{-1}$) and E_i is the photon irradiance of the ionizing laser ($\text{photons cm}^{-2} \text{ s}^{-1}$). Also, A_{21} is the Einstein coefficient for spontaneous emission, B_{12} is the Einstein coefficient for stimulated absorption and B_{21} is the Einstein coefficient for stimulated emission. The rate

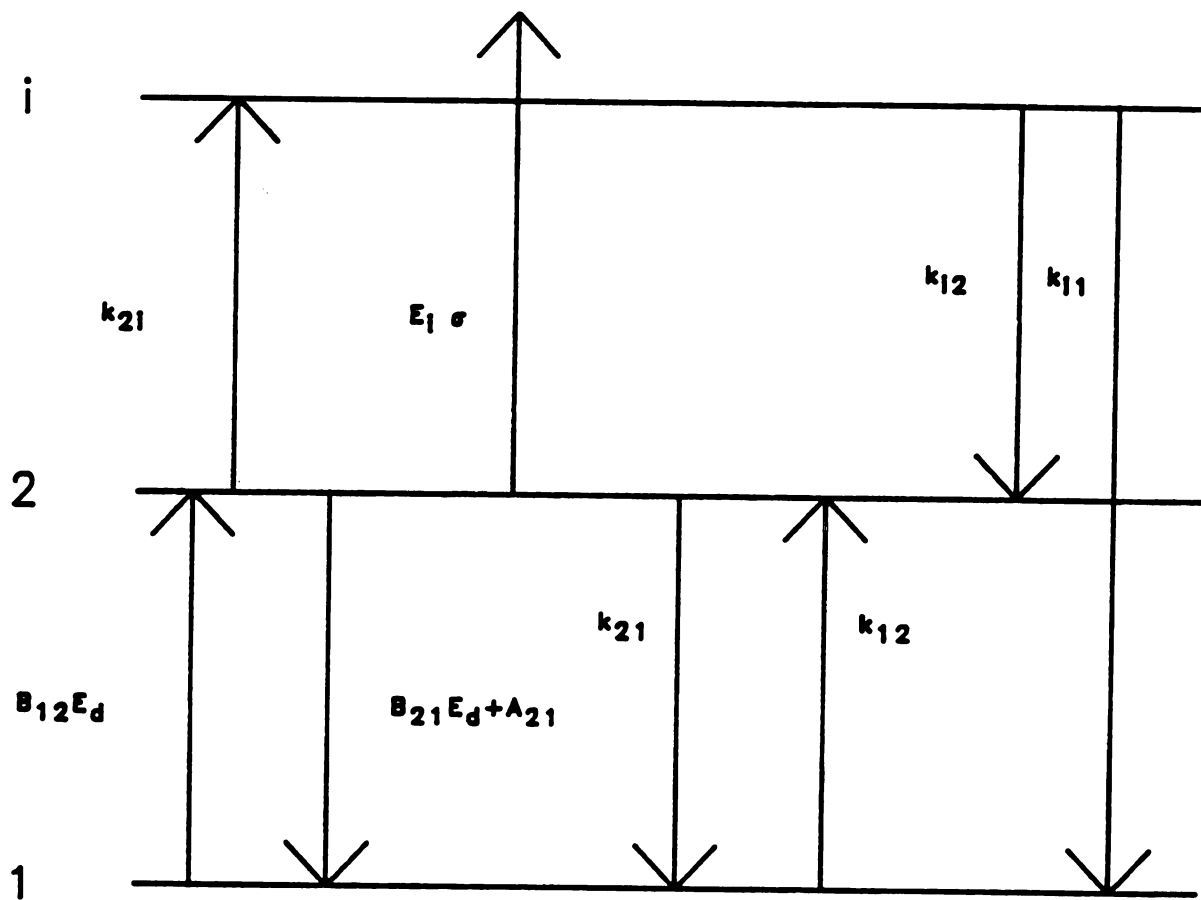


Figure 3 - 1 Atomic Level Scheme - showing transitions for LII experiments.

constant for collisional transfer of population from level i to level j is k_{ij} while σ is the photoionization cross section (cm^2). The rate equations describing this system can then be written:

$$(dn_1/dt) = n_2 (B_{21} E_d + A_{21} + k_{21}) - n_1 (B_{12} E_d + k_{12}) + n_i k_{i1} \quad (1)$$

$$(dn_2/dt) = n_1 (B_{12} E_d + k_{12}) - n_2 (B_{21} E_d + A_{21} + k_{21} + k_{2i} + \sigma E_i) + n_i k_{i2} \quad (2)$$

$$(dn_i/dt) = n_2 (k_{2i} + \sigma E_i) - n_i (k_{i1} + k_{i2}) \quad (3)$$

Many simplifying assumptions can be made to ensure that the model is not too complicated to allow fitting with a reasonable number of data points. The three assumptions are reasonable for the LII experiments being modeled.

1) neither photoionization nor collisional ionization deplete the excited state significantly ($B_{12} E_d + A_{21} + k_{21} \gg \sigma E_i + k_{2i}$)

2) the collisional excitation rate is negligible compared to the absorption rate ($B_{12} E_d \gg k_{12}$).

3) recombination is negligible (this is justified in chapter IV).

The rate equations then simplify to

$$(dn_1/dt) = n_2 (B_{21} E_d + a) - n_1 B_{12} E_d \quad (4)$$

$$(dn_2/dt) = n_1 B_{12} E_d - n_2 (B_{21} E_d + a) \quad (5)$$

$$(dn_1/dt) = n_2 R_1 \quad (6)$$

where $a = A_{21} + k_{21}$ and $R_1 = \sigma E_1 + k_{21}$. If the excited state population can be assumed to achieve a steady state, the population of level 2 at steady state is given by

$$n_2(ss) = n_T \frac{(B_{12}) E_d}{b (E_d + E_s)} \quad (7)$$

where $n_T = n_1 + n_2$, $b = B_{12} + B_{21}$ and $E_s = a/b$. There are two limiting cases of this result. First, in the limit of low irradiances ($E_d < E_s$), $n_2(ss) = n_T B_{12} E_d / E_s$. In the limit of high irradiances $n_2(ss) = n_T B_{12} / b$. These results allow the modeling of limiting cases of the LII signal with the following equation which is derived from the integral of equation (6)

$$n_1 = k E_d E_1 \quad \text{at low irradiances} \quad (8)$$

and

$$n_1 = k E_1 \quad \text{at high irradiances} \quad (9)$$

where k is the collection of all the constants R_1 , n_T , etc. except the irradiances. E_1 is dropped from equations (8) and (9) for experiments in which collisional ionization is predominant. For the experiments modeled in this chapter, the ionizing photon is from the same laser as the exciting photon so that equation (8) becomes $n_1 = k E_d^2$. This model can be used for cases where the exciting or ionizing transitions

are multiphoton. Assuming that no saturation of these transitions occurs the model is $n_i = kE_d^n E_i^m$ where n and m are the number of photons in the exciting and ionizing transitions respectively. In order to develop a general model for the case of the ionizing and exciting laser being the same, the ion population is assumed to follow the equation, $n_i = kE_d^n$. This allows the modeling of multiphoton processes as well as saturated excitations. A similar model can also be assumed to apply to background laser-induced ionization in the flame. While this background can be subtracted from the observed signal, the noise in the background signal remains as part of the total noise. Therefore, it must be considered in any model of the noise in an experiment where it is present.

There are three sources of noise that need to be considered: noise in the analyte signal, noise in the background signal and noise in the zero measurement. The latter is the noise observed with the laser beam blocked. For normally distributed noise, the total noise in a function of several variables $f(x_i)$ can be written in terms of the partial differentials and the variance of the variables

$$\sigma_T^2 = \sum_i (\partial f / \partial x_i)^2 \sigma_{x_i}^2 \quad (10)$$

where σ_{x_i} is the standard deviation of x_i and σ_T is the total standard deviation in the function, f , which in this

case is the signal. For this model, the following signal and background equations will be assumed:

$$\text{signal} = kP^n \quad \text{and} \quad \text{background} = k'P^m \quad (11)$$

where the irradiance E has been replaced with the laser power. It is understood that the area of the laser beam and its spectral width are constant throughout these experiments.

From (10) and (11) an expression for the noise in an LII signal can be written. The shot noise terms in the following equation have been ignored because they do not contribute significantly to the noise at any point. Calculation of the shot noise terms in the signal show that at the point where they equal the zero noise the flicker noise terms in the equation have already dominated. The shot noise terms for LII experiments in flames were calculated to be less than 1% for most elements at their detection limits, because of the zero noise terms. The resulting equation is

$$\sigma_T^2 = (n^2 k^2 \alpha^2 + \sigma_k^2) P^{2n} + (m^2 k'^2 \alpha^2 + \sigma_{k'}^2) P^{2m} + \sigma_{\text{zero}}^2 \quad (12)$$

where σ_{zero} is the standard deviation in the zero measurement, and σ_k and $\sigma_{k'}$ are the standard deviations in the constants k and k' respectively. In equation (12), σ_P , the standard deviation of the laser power, is assumed to be

given by $\sigma_P = \alpha P$, where α is the relative standard deviation of the laser power. Equation (12) is a complex expression for the noise in a laser induced ionization experiment; however, it can be simplified with one assumption. The first term in equation (12) can be rewritten as $(n^2 \alpha^2 + \beta^2) k^2 P^{2n}$ by letting $\sigma_k = \beta k$. For the experiments being modeled in this chapter, the value of α is large, 0.15 to 0.20, so that $n\alpha > \beta$. The value of α was obtained from measurements of the power of individual laser pulses. The value of β is reduced because the ion signal is the total ion current from the flame volume intercepted by the laser beam. This averages out small fluctuations due to flame flicker at a given region in the flame. The first term in equation (12) can be reduced to $n^2 \alpha^2 k^2 P^{2n}$ given that $n\alpha > \beta$. Similarly the second term can be reduced to $m^2 \alpha^2 k'^2 P^{2m}$, so that (12) can be rewritten.

$$\sigma_T^2 = n^2 \alpha^2 k^2 P^{2n} + m^2 \alpha^2 k'^2 P^{2m} + \sigma_{\text{zero}}^2 \quad (13)$$

Equation (13) would still be a complicated expression to fit from a single series of measurements in which only the laser power is varied. However, equation (13) may be broken down into its components. The zero noise can be measured by measuring the standard deviation of the observed signal with the laser blocked. It includes amplifier noise, Johnson noise, and shot noise in the d.c. flame current. The other two terms can be obtained separately as follows.

At each laser power used, the signal and its standard deviation are measured for one solution with analyte and one solution which does not contain the analyte. The first term in equation (13) can be dropped for the case of the solution without analyte. In this way m and k' can be obtained from curve fitting the data for the solutions without analyte. These values are then substituted into equation (13) and the best-fit values of n and k are obtained for the solutions with analyte.

2. Fitting the Data to Model Parameters

Two atomic systems, shown in Figure 3-2, will be studied to test the accuracy of the model for collision and photon dominated ionization schemes. For Na in the excited state, ionization is predominantly collisional. The cross section for absorption of another photon to ionize the atom is too low to compete with collisional ionization when the state is less than 1 eV from the ionization threshold. The reason is that the photoionization cross section decreases rapidly with increasing photon energy above the ionization threshold. For Mn, photoionization predominates due to the large energy difference between the excited state and ionization threshold.

Data points were taken without averaging so that each data point consisted of the integrated ion current for one laser pulse. This was done to ensure that averaging would

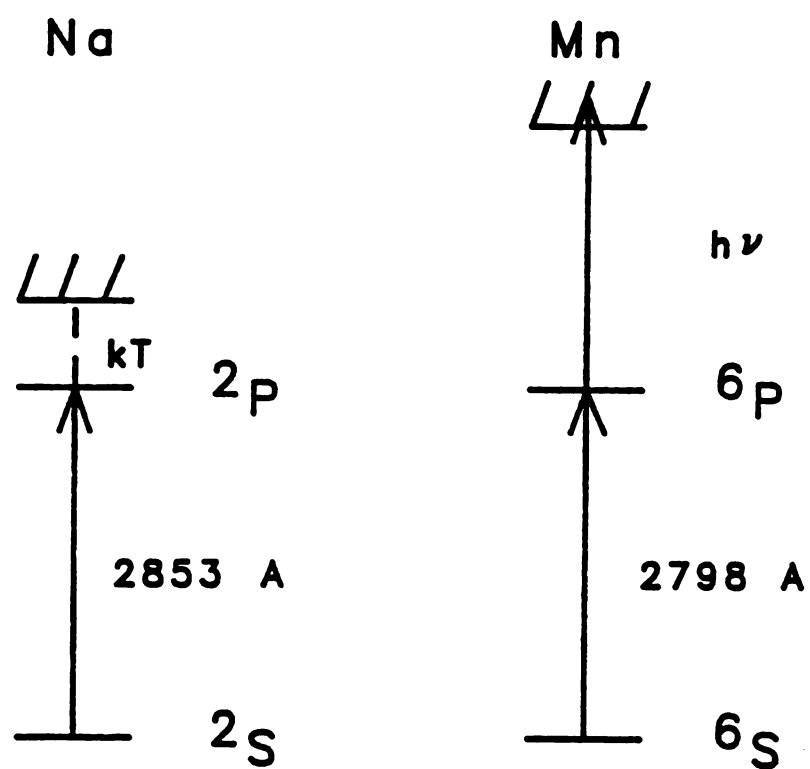


Figure 3 - 2 Energy Levels for Mn and Na - showing states and excitation wavelengths used in these experiments.

not distort the data in any way and no assumptions would have to be made about the effect of the averaging on the characteristics of the noise (e.g., does the noise follow a normal distribution). The gate width used was kept at 250 ns to ensure that the entire electron pulse was integrated and that any time jitter in the triggering circuits would not move any portion of the electron pulse out of the gate open time range. Signals were measured for five hundred laser shots for each solution at each laser power and for the laser-blocked zero measurement. The average of the five hundred points was used as the signal value and the standard deviation of those points was taken as the noise.

There are two ways to obtain the parameters for the noise model. The values of n and k or m and k' can be obtained from fitting the analyte signal or background signal magnitude as a function of laser power [e.g., a log signal versus log relative laser power would give a slope equal to $n(m)$ and an intercept equal to $\log k(k')$]. The other method, as discussed above, involves fitting the noise versus relative laser power data to the total noise model. Where the two methods gave different results, the values from curve fitting of the noise were used because this model was used to derive the signal to noise ratio model. To fit the signals, a linear least squares fit of a log signal versus log relative laser power plot was used, and the slope and intercept obtained. For fitting of the noise, a more complex method was used. To fit the noise to equation (13)

a simplex algorithm, supplied by Peter Wentzell (102), was used.

The simplex method works by minimizing the sum of the squares of the residuals (s.s.r.), the differences between the values calculated by the model and the experimental values. In this case the simplex takes the values for the standard deviation of a measurement as a function of laser power and compares them with the values predicted by the model, equation (13). Next, the simplex calculates two more predictions by changing the values of one or more of the parameters. The simplex then compares the s.s.r. of the three points. It moves away from the worst point and toward the two best points on the s.s.r. versus parameter values surface. The simplex continues incrementing parameters based on the best or worst fit criterion until it can no longer decrease the s.s.r. (i.e., when it has achieved the best fit). The program then returns the final values of the parameters and the sum of the squares of the residuals.

The simplex algorithm was used to fit the standard deviation of the signal as a function of relative laser power. The highest laser power used for a given set of data was assigned a value of 1.0. The same was done for the linear least squares fit of the log signal versus log relative laser power data. Figures 3-3 and 3-4 show the log-log plots of the background signal and Mn signal versus relative laser power for the premixed C₂H₂/air flame. The background signal in this region of the spectrum (≈ 280 nm)

comes from a resonance-enhanced, two-photon ionization of NO (81). NO is formed in high temperature flames when N₂ and O₂ are present. Table 3-1 shows the least squares values of n and k for Mn and Na transitions obtained from the signal versus laser power plots. The parameters n and k were also determined with the simplex method and a fit of the noise versus laser power data. The fits were done in the following manner. First, the standard deviation of the zero level (σ_{zero}) was measured. Then this σ_{zero} value was used in the model for the noise (standard deviation) in the background signal

$$\sigma_{back} = [m^2 k'^2 \alpha^2 P^{2m} + \sigma_{zero}^2]^{1/2} \quad (14)$$

Equation (14) was used to fit the standard deviation of the ionization signal measurements taken with no Mn being aspirated into the flame. From the fit of background noise versus laser power, the values of m and k' were obtained. These values were used in the model for the total noise, equation (13). This model was fit to the Mn ionization signal standard deviation versus laser power data to obtain the values of n and k. Figures 3-5 and 3-6 show the results of fits for the background and the Mn signal in the premixed C₂H₂/air flame. The fit is better for the background noise than for the total noise. This is expected because the model for the total noise uses the parameters m and k' from the fit of the background noise so that any lack of fit from

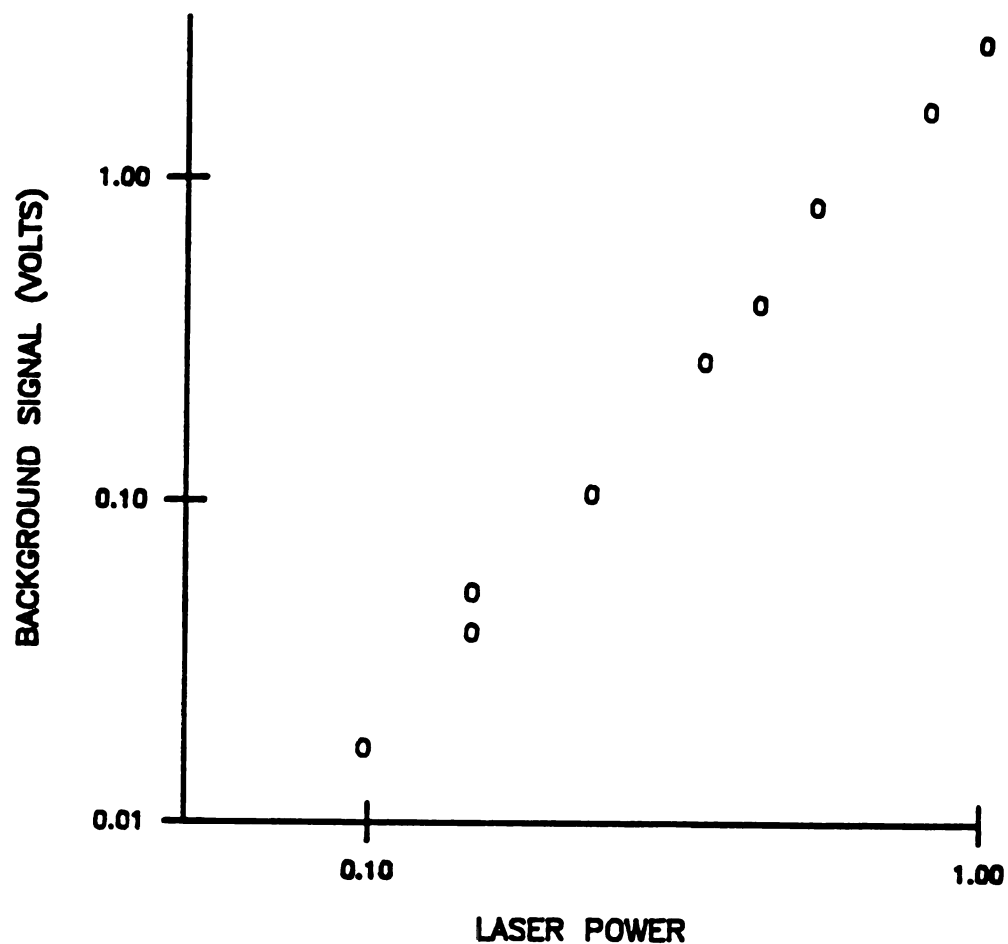


Figure 3 - 3 Power Dependence of the Background Signal measured at the Mn excitation wavelength in the C₂H₂/air flame.

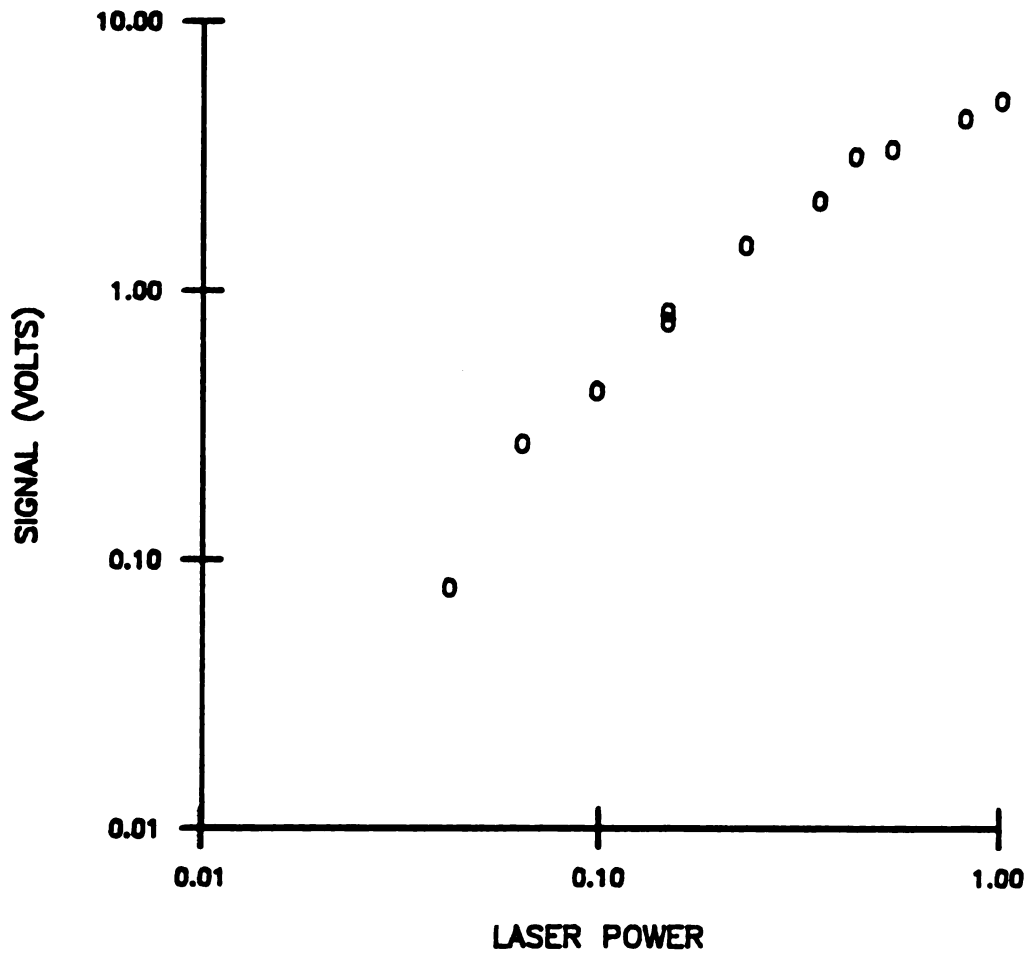


Figure 3 - 4 Power Dependence of the Mn Signal measured in the C₂H₂/air flame.

Analyte	Wavelength (Å)	Flame	PD	Coefficient	P _{max}
background	2798.3	C ₂ H ₂ /air	2.3	2.83	900
Mn			1.2	8.22	
back.	2853.0		2.0	0.38	750
Na		H ₂ /O ₂ /Ar	0.7	5.38	
back.	2798.3		1.9	2.50	900
Mn			1.1	2.03	
back.	2845.5		1.8	6.7	700

Table 3 - 1 Power Dependences and Coefficients from fits of the signals to the kP^n model. PD = the power dependence exponent, n. P_{max} = laser irradiance (kW cm⁻²) assigned the value 1.0.

the first model is carried over into the fitting for the total noise model. Table 3-2 shows the parameters from the fits of the noise in Mn and Na signals for the C₂H₂/air and H₂/O₂/Ar flames.

Two important parameters in the table which describe how well the data fit the model are the sum of the squares of the residuals (s.s.r.) and the standard error of the estimate (s.e.e.). The s.s.r is the sum of the squares of the differences between the observed $(\sigma_T)_i$ and predicted $(\sigma'_T)_i$ values of the standard deviation.

$$\text{s.s.r.} = \sum_i [(\sigma'_T)_i - (\sigma_T)_i]^2 \quad (15)$$

The standard error of the estimate is given by

$$\text{s.e.e.} = (\text{s.s.r.}/(n-r))^{1/2} \quad (16)$$

where n is the number of points and r is the number of parameters fit. For most modeled systems it is possible to use the s.e.e. to test how well the model fits the data. If the s.e.e. is approximately equal to the standard deviation of the experimental measurements then the model is as good as the data. In this case, however, because the parameter being modeled is the standard deviation it is not possible to know the standard deviation of the modeled data so the comparison mentioned above is not possible.

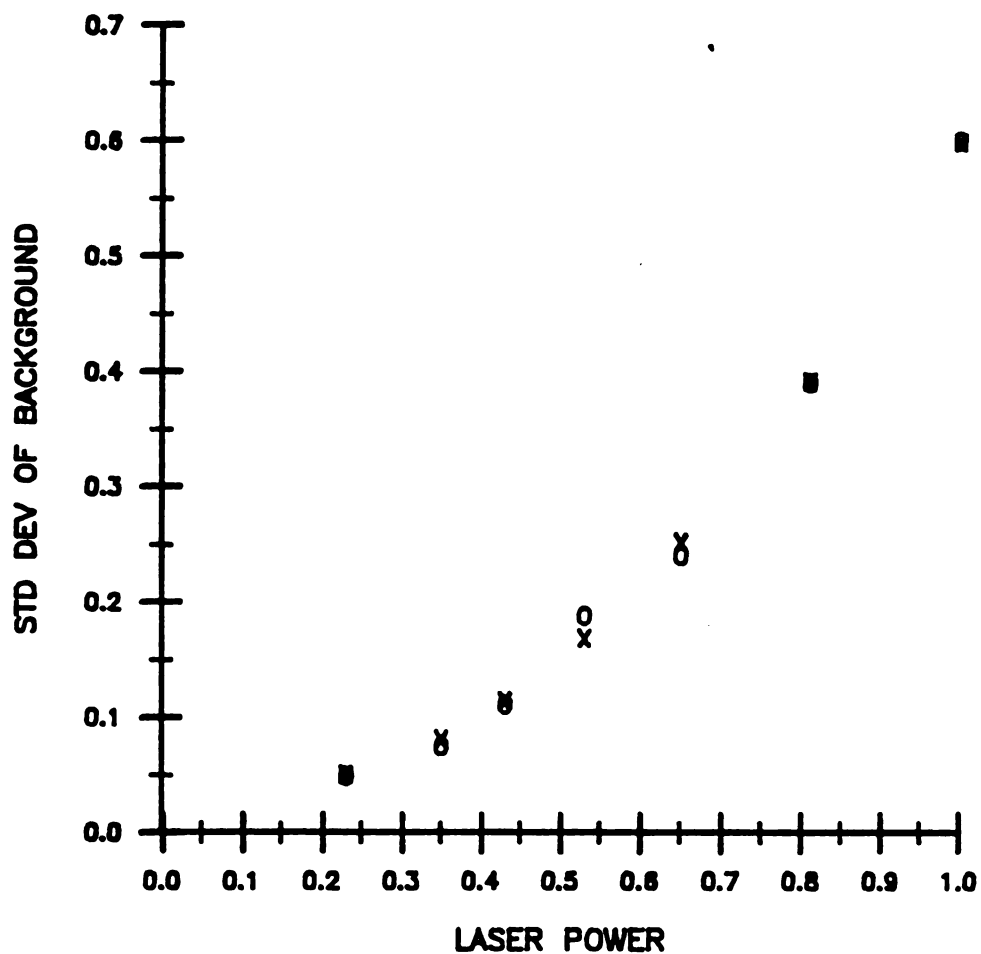


Figure 3 - 5 Fit of the Background Noise to the Model o - are experimental data points x - are the fitted model's results.

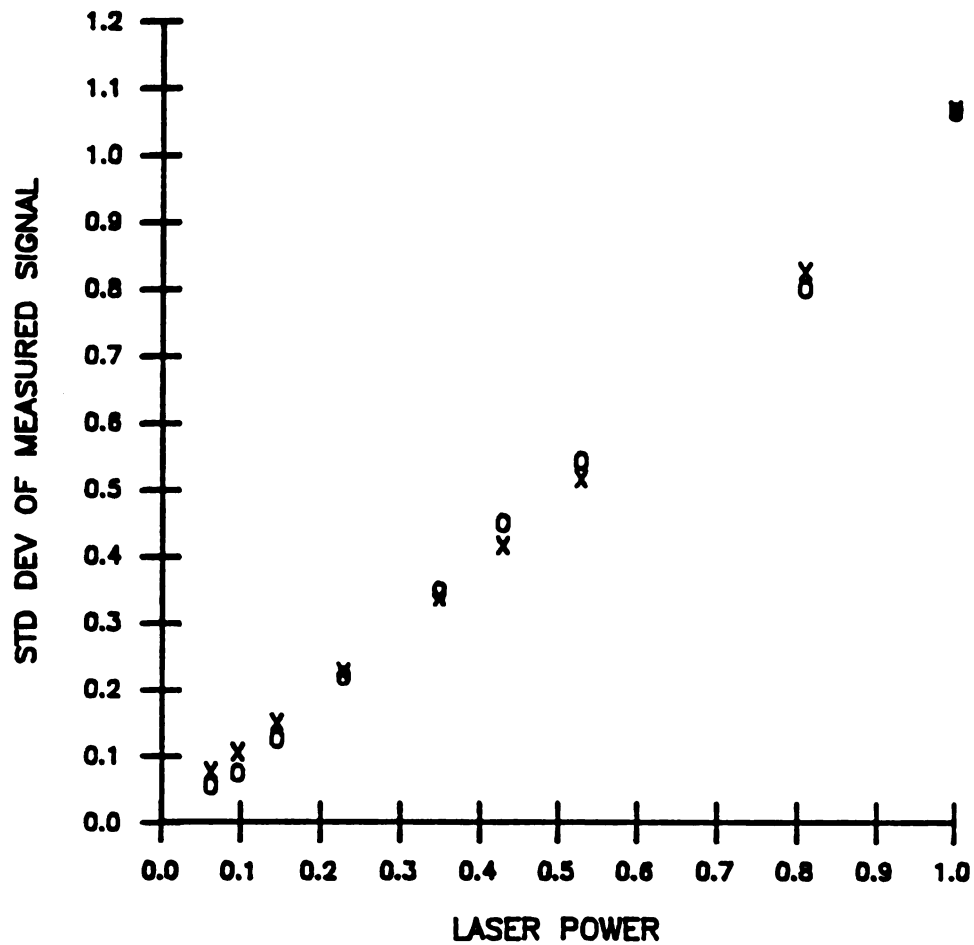


Figure 3 - 6 Fit of Total Noise in Mn Signal o - are experimental points and x - are fitted points.

flame	Anal.	n	m	k(V)	k'	s.s.r.	s.e.e.	$P_{\max}$	P_{opt}
								(kW cm ⁻²)	
C ₂ H ₂ /air	Mn	1.0	2.0	4.68	1.47	3.1×10^{-3}	0.026	900	250
	Na	0.7	2.7	3.07	0.33	2.6×10^{-3}	0.023	750	200
H ₂ /O ₂ /Ar	Mn	1.0	2.0	2.58	1.50	1.4×10^{-2}	0.040	900	120
	back.		1.7		5.4	6.6×10^{-4}	0.015	400	

Table 3 - 2 Parameters from the noise fits. $P_{\max}$ is the laser irradiance assigned a relative value of 1.0.

3. Predictions of the Model

The parameters obtained from the fits can be used to optimize experimental conditions or to predict the effect of changes in experimental parameters on the signal-to-noise ratio for an ionization measurement. The fact that the background power dependence is greater than the analyte signal's and that there is a nonzero zero noise means that there will be a maximum in the signal-to-noise ratio versus laser power curve. The models described above can be used to predict the position of this maximum by writing the expression for the signal-to-noise ratio and setting the derivative with respect to laser power equal to zero. The result is

$$P_{opt}^2 = \frac{\sigma_{zero}^2}{[(m/n)-1](m^2 k'^2 \alpha^2 + \sigma_{k'}^2)} \quad (17)$$

where P_{opt} is the laser power for maximum signal-to-noise ratio. As before, if the flame flicker noise, $\sigma_{k'}$, is small relative to the laser power noise, it may be neglected.

Table 3-2 lists the optimum laser power calculated for each analyte/flame system studied. Because shot noise terms are not included in equation (17), the optimum power does not depend strongly on the analyte parameters. What equation (17) does show is the importance of the zero noise and the background signal noise and their opposing effects

on P_{opt} . It is useful to know how critical it is to be at the optimum power, i.e., how quickly the signal-to-noise ratio decreases on either side of the optimum as a function of laser power.

Figure 3-7 shows the calculated signal-to-noise ratio for a 1 ppm Mn solution aspirated into an C_2H_2 /air flame as a function of laser power. The optimum signal-to-noise ratio occurs for a relative laser power of 0.15 where 1.0 is the maximum power used (≈ 700 kW/cm²). The signal-to-noise ratio decreases rapidly for laser powers less than 1/2 of the optimum because of the increasing importance of the zero noise term. The decrease in signal-to-noise ratio at higher laser powers is due to the background noise term, which increases more quickly with laser power than the signal. The rate of decrease at high laser powers is controlled by the background power dependence, m , and the sensitivity, k' . The effect of k' on the signal-to-noise ratio versus laser power curves and the optimum laser power can be seen in Figures 3-8 and 3-9 and equation (17). Equation (17) shows that the optimum laser power decreases with increasing sensitivity of the background signal. In Figure 3-8 the signal-to-noise ratio curves are plotted. Parameters from the fit of the noise in the Mn signal in the C_2H_2 /air flame are used, but the value of k' is varied. Variation of k' could occur when changing flames, due to increasing or decreasing amounts of the background species in the flame. The value of k' can be increased by introducing sample

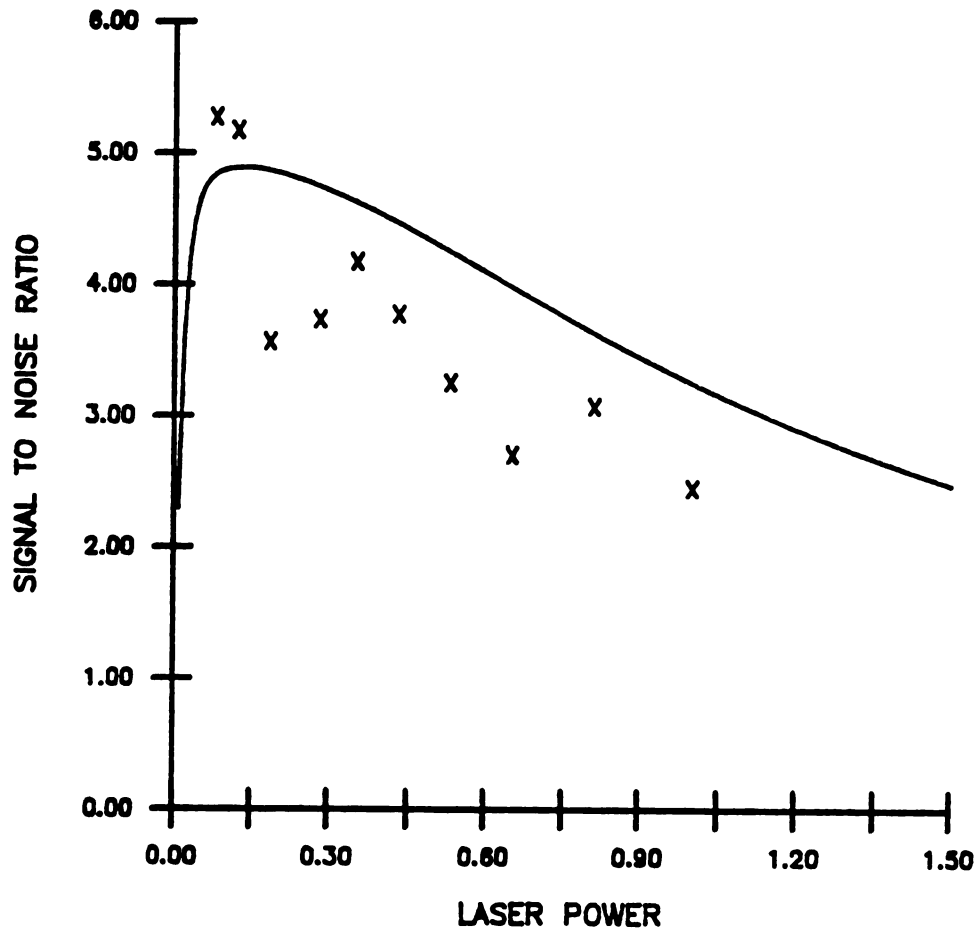


Figure 3 - 7 Predicted Signal to Noise Ratio vs. Laser Power - x - are experimental points, and the line is the predicted value from the model parameters.

matrices which contain species which can be more easily ionized than the flame species or when increasing the gain of amplifiers to observe lower concentrations of analyte. The best obtainable signal-to-noise ratio is determined primarily by the relative standard deviation of the laser power but the value of k' determines how quickly the signal-to-noise ratio decreases with increasing laser power. The observed case for 1 ppm Mn in the C_2H_2 /air flame is the center curve in Figure 3-8. If the background sensitivity, k' , is 10% of the signal sensitivity, k , the signal-to-noise ratio stays very constant out to high laser powers (>10 MW/cm²). The species responsible for the background ionization signal is NO. As k' increases, the rate of decrease in signal-to-noise ratio with increasing laser power increases, and the optimum laser power decreases, as predicted by equation (17). The signal-to-noise ratio at the optimum laser power also decreases slightly. So, if the laser is operated in the correct power range, the effect of increasing background on the signal-to-noise ratio can be minimized. The range of laser powers that can be used without significantly lowering the signal-to-noise ratio narrows considerably with increasing k' . This becomes important at low concentrations (small k) when the value of k' can equal or surpass the value of k . Under these conditions, the laser power used can be critical in determining the precision of the measurement. Figure 3-9 shows the same curves for the case of 2 ppm Na aspirated

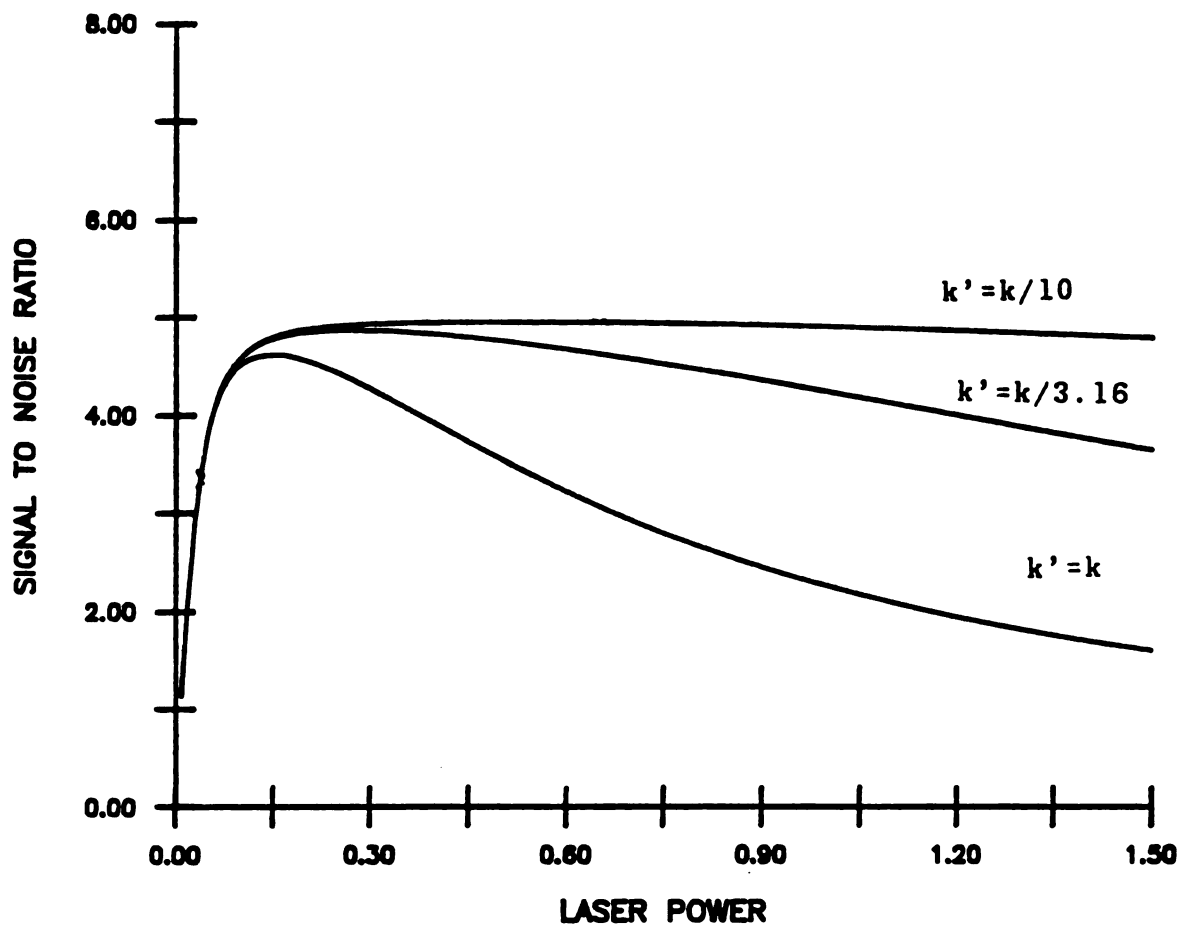


Figure 3 - 8 Effect of Background Sensitivity on S/N
Other parameters taken from the Mn - C₂H₂/air system.

into the same C_2H_2 /air flame. This is an interesting case because of the partial saturation of the Na transition. The lower power dependence makes the analyte signal less sensitive to laser power fluctuations than the Mn signal which had a power dependence of 1. This increases the maximum signal-to-noise ratio. The curves are also noticeably flatter near the optimum signal-to-noise ratio, but the values decrease more rapidly at higher laser power due to the decreased value of n with respect to m . The Na signal increases more slowly with laser power than the Mn signal; therefore, the background noise overtakes it more quickly than in the Mn case.

The effect of the signal power dependence, n , can be seen in Figure 3-10. The three curves are for $n = 0$, 1, and 2. All other parameters used are from the 1 ppm Mn- C_2H_2 /air flame system. When multiphoton transitions with no saturation are used (e.g., the lower curve with $n=2$) the obtainable signal-to-noise ratio decreases significantly because the $n > 1$ power dependence multiplies the laser power noise. For $n > m$ the laser power for optimum signal-to-noise ratio approaches infinity. Although this case is not likely to be used analytically it is interesting to contemplate. The center curve, $n = 1$, is the observed case. Because $n < m$ there is an observed maximum in the signal to noise ratio versus power curve. If the analyte transition is completely saturated, $n = 0$, the optimum laser power approaches zero. Of course, the optimum power can not be

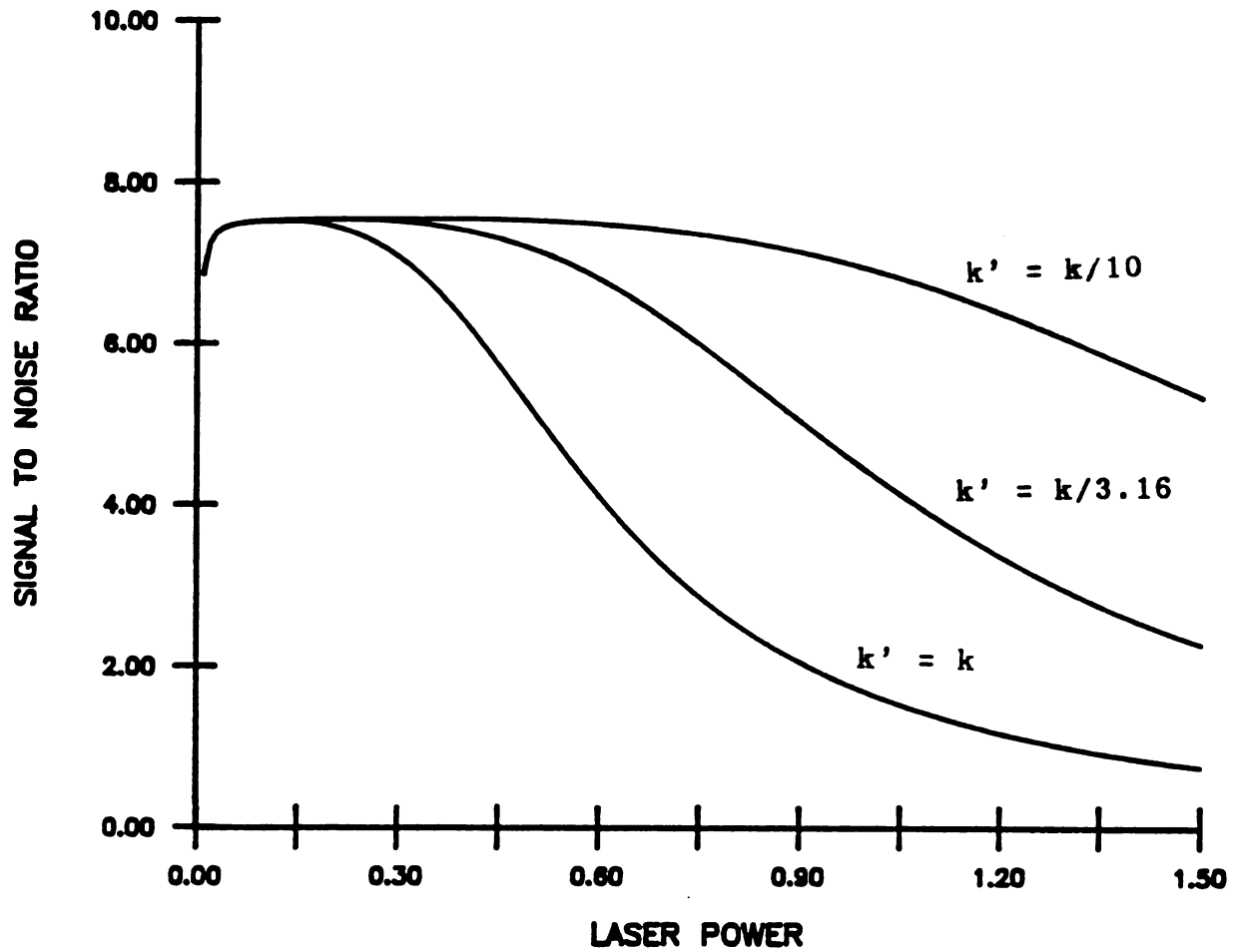


Figure 3 - 9 Effect of Background Sensitivity on S/N other parameters taken from the Na-C₂H₂/air system.

zero because the transition would no longer be saturated. The signal-to-noise ratio increases greatly when the analyte transition is saturated because this decreases the dependence of the total noise on the laser power noise. Figure 3-10 shows the advantages of strong transitions (those with large dipole moments) in LII. Strong transitions are easy to saturate at low powers so that background noise is small and laser power noise has less effect, so that high precision results.

The relative standard deviation (RSD) of the power of the laser pulses is an important parameter in determining the signal-to-noise ratio. As noted above the RSD of the laser power was approximately 0.2 at the wavelengths used in these experiments. The reason for this rather large RSD is the number of nonlinear and pump processes which must be used to produce tunable ultraviolet radiation. Each adds to the noise in the laser output. When only visible radiation is necessary for the excitation and ionization processes the laser power RSD decreases by a factor of about 2. The reason for the decrease is that nonlinear crystals which are used to frequency double the output of the dye laser to create ultraviolet radiation are not used at visible wavelengths. The effect of laser RSD is approximately multiplicative, as shown in Figure 3-11. As the RSD of the laser power decreases, the signal-to-noise ratio increases by approximately that amount except near zero power where the zero noise is the predominant noise source. The laser

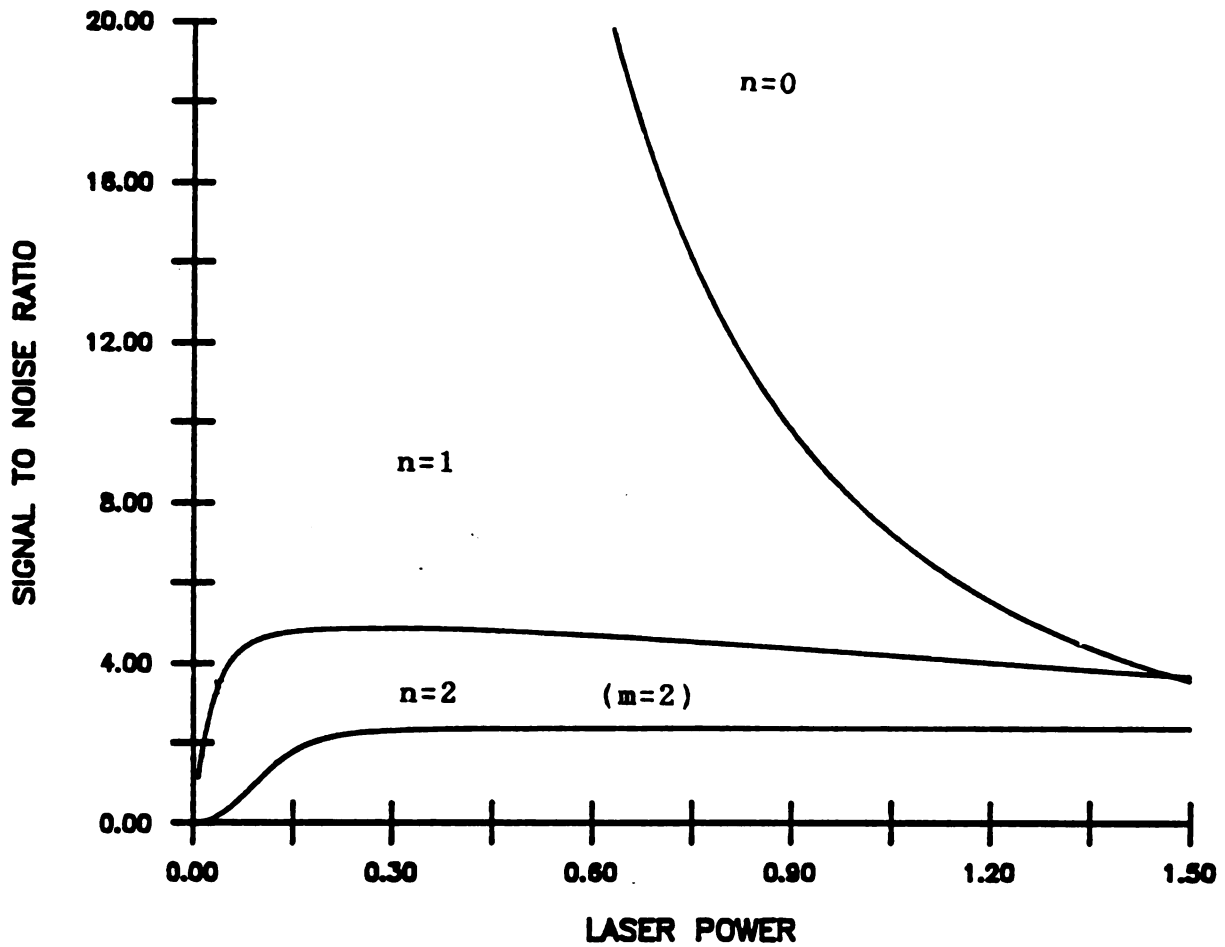


Figure 3 - 10 Effect of Signal Power Dependence on S/N other parameters taken from the Mn-C₂H₂/air system.

power for optimum signal-to-noise ratio decreases with increasing laser power RSD so that higher power could be used in the visible to saturate weak transitions without sacrificing precision.

B. An Extended Model

The models presented in the previous section work well for weakly pumped transitions and for saturated transitions. However, the system under study is often only partially saturated. For these cases it is necessary to modify the model so that the partial saturation can be described with accuracy. Equation (7) describes the behavior of the excited state population in the steady state-limit. The noise model can then be derived in the same manner as it was in Section A of this chapter. With the more general excitation model, three different cases are considered for the noise model derivation: a), a photoionization experiment where the ionizing photon is from the same laser as the exciting photon; b), a photoionization experiment where the ionizing photon is from a different laser; and c) an experiment where collisional ionization predominates over photoionization. The extended model for case c) is applied to the data for the Na system modeled in Section A because this system exhibits significant partial saturation and is the most likely to be affected by the assumptions of the previous model.

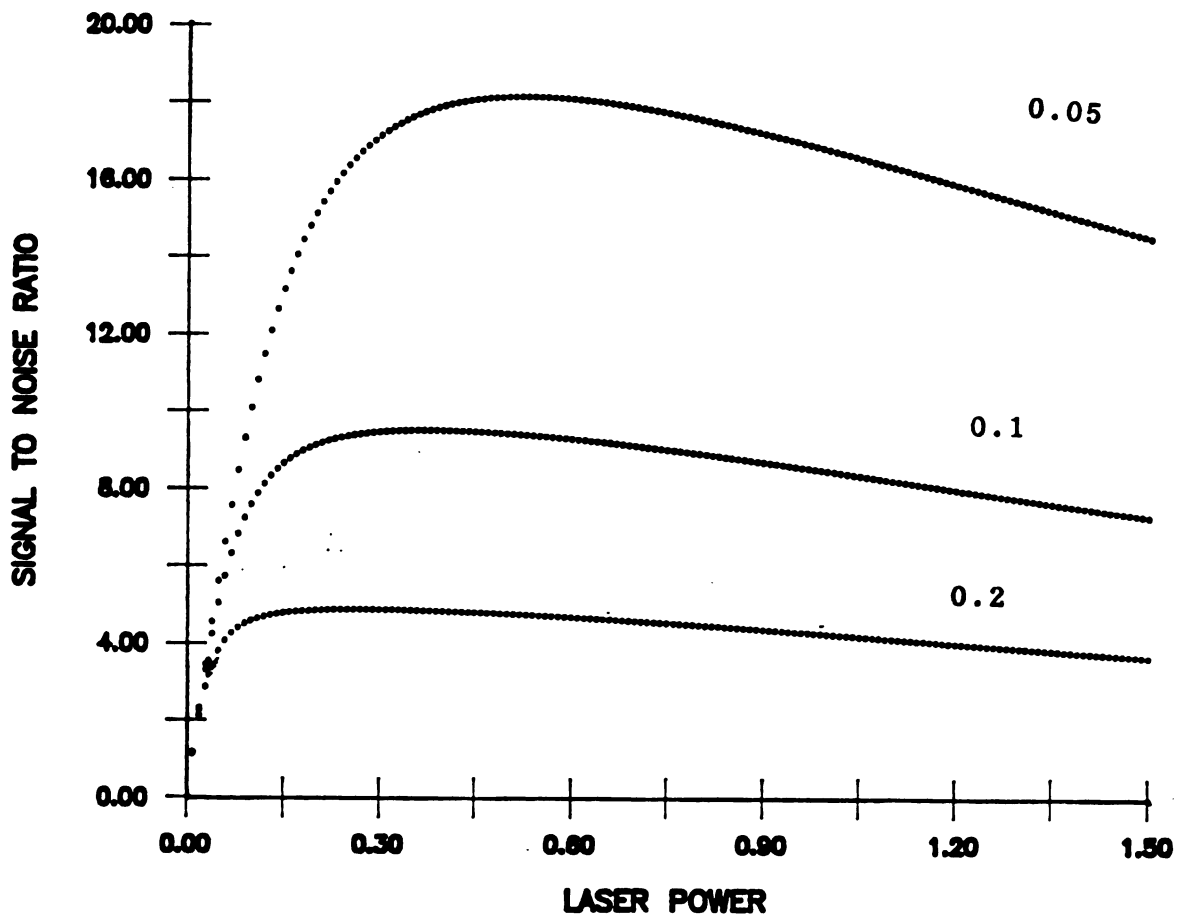


Figure 3 - 11 Effect of Laser Power R.S.D. the numbers to the side are the laser power r.s.d. other parameters taken from the Mn-C₂H₂/air system.

1. Derivation of the Model

a. Case a): Single laser, resonance-enhanced photoionization

The new extended model for the LII signal is $\text{signal} = kP_d P_i / (P_d + P_s)$. For the case of a single laser photoionization experiment the final form is

$$\text{signal} = kP_d^2 / (P_d + P_s) \quad (18)$$

By using equation (10) one obtains the following expression for the noise in the analyte signal only (not including background and zero noise terms)

$$\sigma_{\text{anal}}^2 = \frac{k^2 P^2 \sigma_P^2}{(P + P_s)^2} + \frac{P^2 \sigma_k^2}{(P + P_s)^2} \quad (19)$$

note that the subscript has been dropped from the dye laser power in equation (19). Recall that the total noise observed is given by $\sigma_T^2 = \sigma_{\text{anal}}^2 + \sigma_{\text{back}}^2 + \sigma_{\text{zero}}^2$. The observed power dependence will determine whether the model for the background noise is best drawn from this section or Section A. If the substitutions $\sigma_P = \alpha P$ and $\sigma_k = \beta k$ are made in equation (15), the following simplification results

$$\sigma_{\text{anal}}^2 = \frac{k^2 P^4}{(P + P_s)^2} \left[\frac{(P + 2P_s)^2}{(P + P_s)^2} \alpha^2 + \beta^2 \right] \quad (20)$$

Again if $\alpha > \beta$ the term with β^2 can be neglected.

b. Case b) : Two laser photoionization experiments

The extended model for case b) is

$$\text{signal} = k P_d P_i / (P_d + P_s) \quad (21)$$

If equation (10) is applied, the result is

$$\sigma^2_{\text{anal}} = \frac{k^2 P_d^2 \sigma_{P_i}^2}{(P_d + P_s)^2} + \frac{P_d^2 P_i^2 \sigma_k^2}{(P_d + P_s)^2} + k^2 \left[\frac{P_i}{(P_d + P_s)} + \frac{P_d P_i}{(P_d + P_s)^2} \right] \sigma^2_{P_d} \quad (22)$$

or after substituting $\sigma_{P_i} = \alpha_i P_i$, $\sigma_{P_d} = \alpha_d P_d$ and $\sigma_k = \beta k$

$$\sigma^2_{\text{anal}} = \frac{\alpha_i^2 k^2 P_d^2 P_i^2}{(P_d + P_s)^2} + \frac{\alpha_d^2 k^2 P_d^2 P_i^2 P_s^2}{(P_d + P_s)^4} + \frac{\beta^2 k^2 P_d^2 P_i^2}{(P_d + P_s)^2} \quad (23)$$

As in case a), terms for the noise in the background and zero must be added to this expression and the term containing β can be dropped if appropriate.

c. Case c) : Collisional ionization

When collisional ionization dominates over photoionization from the excited state, the model for the signal simplifies to

$$\text{signal} = kP_d / (P_d + P_s) \quad (24)$$

This is the model which describes the Na LII experiment presented in Section A of this chapter. Substituting equation (24) into equation (10), one obtains

$$\sigma_{\text{anal}}^2 = \alpha^2 \frac{k^2 P_d^2 P_s^2}{(P_d + P_s)^4} + \beta^2 \frac{k^2 P_d^2}{(P_d + P_s)^2} \quad (25)$$

The term containing β^2 can be eliminated since $\alpha > \beta$. A model for the background from Section A of this chapter will be used. The resulting expression for the total noise is

$$\sigma_T^2 = \alpha^2 \left[\frac{k^2 P_d^2 P_s^2}{(P_d + P_s)^4} + m^2 k'^2 P^2 m \right] + \sigma_{\text{zero}}^2 \quad (26)$$

2. Fitting the Data to Model Parameters

The simplex method can be used to fit the noise versus laser power data to equation (26) as was shown in section A. First, the zero noise is measured. Then the background only data are fit to obtain m and k' . Finally, the total noise is fit by using the values of m , k' , and σ_{zero} from the previous measurements and fits, to give P_s and k . To obtain a good fit for P_s , a large portion of the saturation curve must be sampled. A number of points must be taken along the linear and bending section of the noise versus laser power curve and some points should be taken in the saturation region. Therefore, the extended model requires more data

for fitting purposes, but it should more accurately describe the data. Figure 3-12 shows the results of fitting the extended model for 2 ppm Na aspirated into the $H_2/O_2/Ar$ flame and the fit of the same data with the model from Section A. The numerical results are tabulated in Table 3-3. Figure 3-12 shows that the simple power dependence model of Section A does not fit the entire power curve from the linear region through the saturation region. However, the extended model fits well over the entire curve. The difference in the fits is also apparent in the differences in the sums of the squares of the residuals and the standard errors of the estimates. Both models were used to fit the same data so the significantly lower s.s.r and s.e.e. for the extended model show that the extended model fits the data better.

3. Predictions of the Extended Model

The parameters from the extended model fit can be used to make predictions about the signal-to-noise ratio for Na determinations. The only difference in parameters for this model is that instead of a power dependence exponent, n , there is the saturation power (irradiance) parameter. The other parameters occur in the same mathematical form as in the previous model and therefore affect the signal-to-noise ratio in the same manner. The effect of the saturation parameter is presented in Figure 3-13. All other parameters

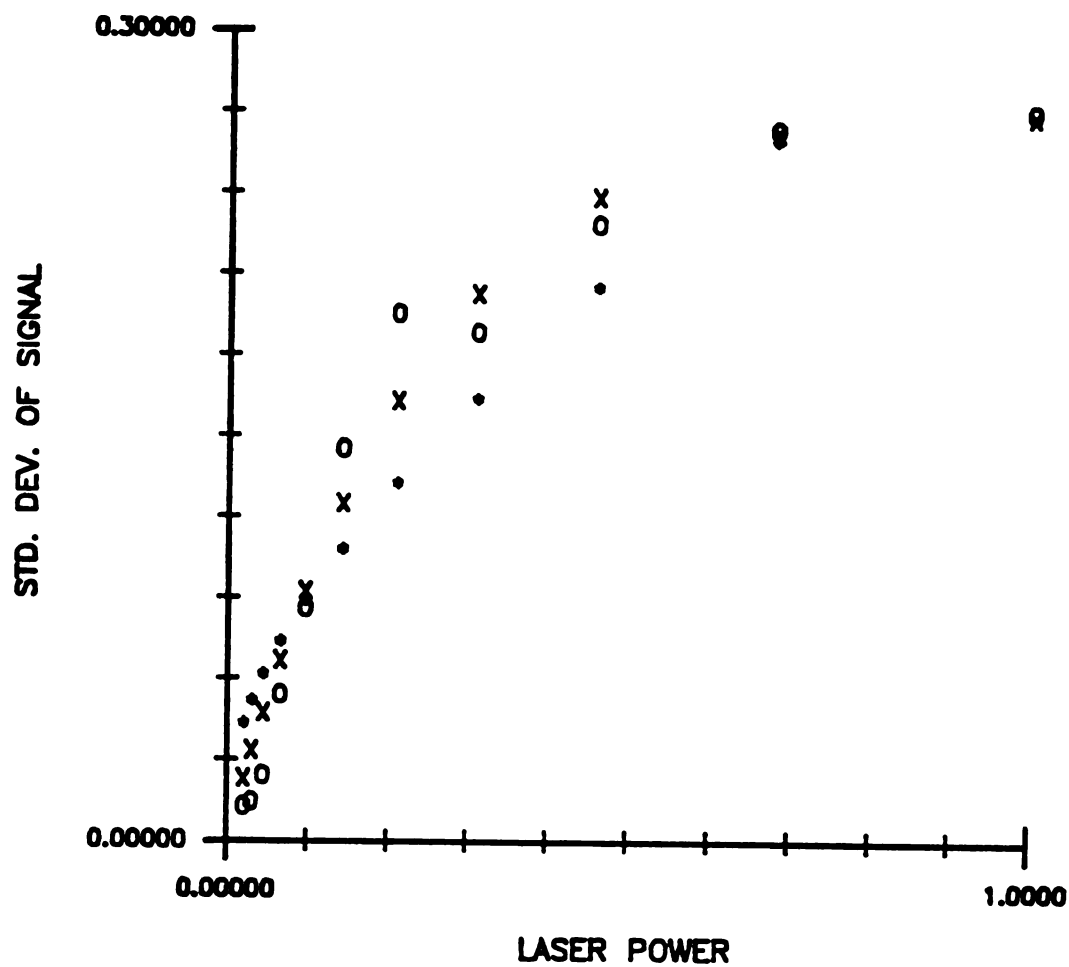


Figure 3 - 12 Fit of the Extended Model to Noise in the Na Signal o - are experimental points, x - are fit points of the extended model * - are fit points of the power dependence model.

<u>Extended Model Parameters</u>		<u>Section A Model Parameters</u>	
k	5.28 V	k	2.56 V
P _s	0.90	n	0.426
s.s.r.	$2.97 \times 10^{-3} \text{ V}^2$	s.s.r.	$1.43 \times 10^{-2} \text{ V}^2$
s.e.e.	0.018 V	s.e.e.	0.040 V

Table 3 - 3 Comparison of the Results of the Two Models
 Note, the same model and parameters for background
 ionization noise was used in both cases.

are held constant at the values for the 2 ppm Na solution aspirated into the H₂/O₂/Ar flame. As the saturation power is decreased (i.e., as stronger transitions are probed) the transition saturates at lower laser powers so that the largest signal-to-noise ratio is obtained at lower powers. The maximum signal-to-noise ratio is also higher for transitions with lower saturation irradiances. This happens because higher signals are obtained at lower powers and the increased saturation decreases the effect of laser noise variations. Cases a) and b) of the extended model have more complex forms, but could be analyzed in similar manners. Case b) requires data to be taken with both laser powers varied in order to find the optimum for both laser powers.

C. Flame Flicker Noise

In the models of Sections A and B when the simplex fitting was done, β , the relative standard deviation of k , was assumed to be small enough relative to α , the relative standard deviation of the laser power, that terms in β^2 could be assumed to be zero. This is reasonable because of the large value of α for the ultraviolet pulses used and because of the integration of $k(k')$ over the volume of the flame intercepted by the laser beam. This section describes the measurement of β which was done to validate the assumptions made concerning its magnitude. It is also useful to know at what value of α the terms in β^2 should be

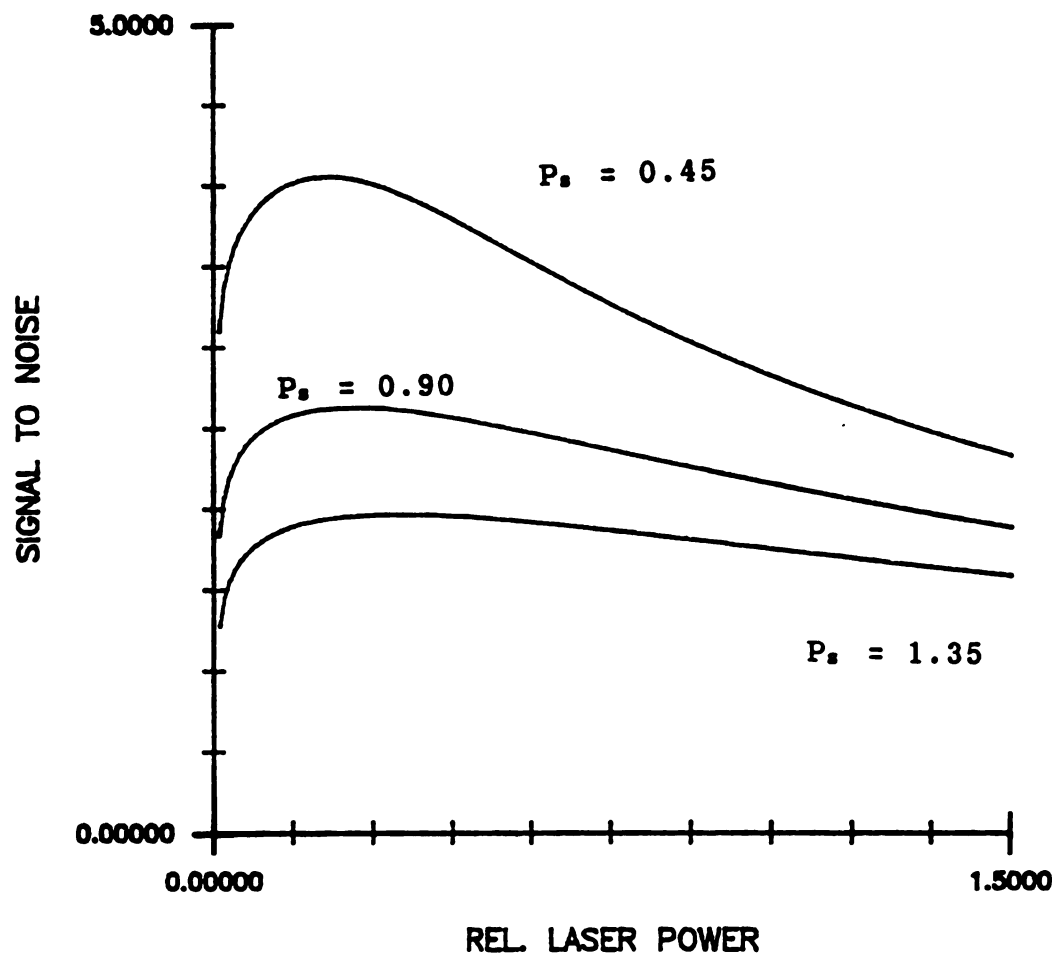


Figure 3 - 13 Effect of the Saturation Irradiance on S/N other parameters from the extended model fit of the Na-H₂/O₂/Ar system.

kept in the model. The relative standard deviation of k for a series of 5 ns gates (laser pulses) repeated at 0.1 second intervals is β . The coefficient, k is a collection of constants which contains factors from the rate equations model for the ionization and parameters from the signal processing equipment (e.g., preamplifier gain). If the instrumental parameters are assumed to be fixed over time, the variation comes from the constants in the rate equations.

The constants from the rate equations are, n_T , the total number density of the probed species; R_i , the total ionization rate constant; B_{ij} , the Einstein coefficients for absorption and stimulated emission. The B_{ij} coefficients are constants so they do not contribute to pulse-to-pulse variations in k ; this leaves only n_T and R_i to be considered. For experiments in which photoionization dominates, the variation is that of the ionizing laser, which has already been incorporated into the models. Thus, only changes in n_T need to be considered for photoionization experiments. Note however, changes in both n_T and k_{21} should be considered for experiments in which collisional ionization dominates.

Measurement of n_T by indirect means is not difficult and will be discussed later in this section; however, measurement of k_{21} is not so easy. Cross sections for the process are constant so only fluctuations in temperature and collision partner number density should change k_{21} . For the

laminar flames used in these experiments these fluctuations should not be significant. However, if measurement of n_r indicates large fluctuations, changes in k_{21} may need to be investigated for collisional ionization experiments. The relative standard deviation of n_r can be measured indirectly by measuring the RSD of emission for a transition of the analyte species. This assumes that temperature does not fluctuate significantly and give a varying Boltzmann distribution. In order to match the RSD from emission measurements to the time frame used for LII experiments, the boxcar integrator was used to gate emission signals. It was triggered at 10 Hz, the laser repetition frequency. A monochromator (series EU 700, McPherson) was used to isolate the emission wavelength of the probed species. A photomultiplier tube (1P28, RCA) was used to produce a current proportional to the emission intensity. The output current of the photomultiplier was converted to voltage and amplified by a fast d.c. electrometer constructed by Christman (125). The minimum rise time (5 microseconds) was used to ensure that the amplifier could follow the fluctuations in emission. Figure 3-14 shows a diagram of the instrument used to measure flame emission and the RSD of the emission for samples taken at 10 Hz.

The RSD of the emission measured was less than 3%. In the cases modeled, where the laser power RSD was $\approx 20\%$ the terms in β^2 can certainly be neglected. For lasers where

the pulse-to-pulse variations have an RSD of less than 10%, these terms should be measured and included.

D. Conclusion

This chapter has presented two models for the noise in LII signals. The first model uses a single exponent to describe the laser power dependence of the analyte or background signals, P^n . This model describes transitions with integer n well. Integer n means that no saturation of the transition probed is observed or that complete saturation is observed. For example, the Mn ionization experiment can be described by this model. The excitation transition is saturated at all laser powers used, and the ionization, which is dominated by photoionization, is not saturated. The result is that the ionization signal noise depends on P^n with $n=1$. For partially saturated transitions this model does not accurately describe experimental observations.

The extended model takes the saturation into account by introducing the saturation power (irradiance) parameter, P_s . The Na ionization experiment is an example of an experiment with a partially saturated transition. The extended model describes the Na system more accurately as shown by its smaller s.e.e. In order to fit the saturation parameter, P_s , accurately, a wide range of laser powers must be sampled. This allows the the saturation curve to be mapped. Both

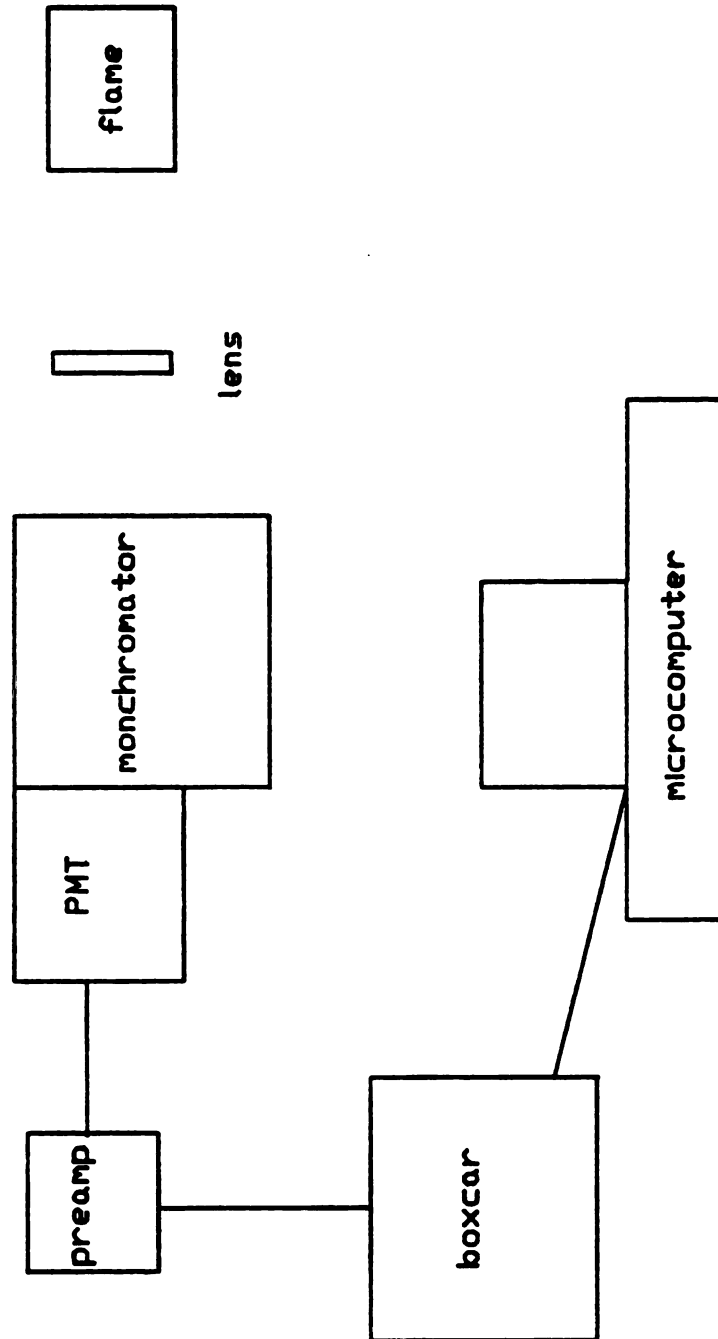


Figure 3 - 14 Experimental System for Emission Measurements

models were developed considering shot noise to be negligible based on calculations which showed the shot noise for flame experiments to be less than 1% RSD. For vacuum chamber experiments, where very small numbers of ions can be detected, the shot noise terms would become important, and the models would have to be rederived. The models were fit to experimental data to obtain the values of the model parameters. After the model parameters had been obtained it was possible to use their values to predict the laser power needed for maximum signal-to-noise ratio and the effect of various experimental parameters on signal-to-noise ratios of LII measurements. The flame flicker RSD was measured and shown to be negligible for lasers whose power fluctuations are greater than 10%.

E. Appendix

This chapter has shown the importance of the background signal in determining the precision of LII measurements. The background ionization usually has a higher order power dependence than the signal and therefore the signal-to-noise ratio decreases at high laser powers. The noise models presented can be used to optimize the signal-to-noise ratio if the background has been characterized. Therefore this appendix will present background spectra and power dependencies for various spectral regions in the two flames

used. These can then be used by experimenters to choose the transitions to use for determinations by LII methods. The determination of high ionization energy elements (I.E. > 6 eV) requires one of the following approaches; the use of high energy photons (ultraviolet) for excitation and ionization; multiphoton processes, or the use of photoionization if visible light is used. For example, stepwise LBI schemes have been used to excite atoms to high-energy excited states, but these schemes require two tunable lasers. Multiphoton excitations through virtual states require high laser irradiances which, as noted before, can cause large background ionization signals with correspondingly high noise levels.

The single laser system used for the experiments reported in this dissertation is simpler and it can ionize species with ionization potentials up to 9 eV with only one resonant exciting and one ionizing photon if ultraviolet excitation is used. Flames contain many species which absorb ultraviolet light; therefore, there is the potential for background ionization and photoionization of sample matrix species is more likely when ultraviolet radiation is directed into the flame.

The background signal observed at the Mn and Na transitions wavelengths is an example of the ionization of flame species. Mallard et al. (81) have observed the resonantly enhanced 2-photon photoionization of NO in an atmospheric pressure $\text{H}_2/\text{O}_2/\text{N}_2\text{O}$ flame over the wavelength

region from 270 nm to 317 nm. In the 280 nm region the head of the (1,6) and the tail of the (0,5) bands of the $X^2\Pi - A^2\Sigma^+$ electronic system are observed. Figure 3-15 is the photoionization spectrum of the $H_2/O_2/Ar$ flame in the region from 280 to 285 nm. This spectrum matches that obtained by Mallard and coworkers. It is also the same spectrum that is observed in the C_2H_2/air flame also used in these experiments. The observed background signal in the $H_2/O_2/Ar$ flame was more sensitive than in the C_2H_2/air flame. The NO in the $H_2/O_2/Ar$ flame was formed from N_2 in the air entrained by the flame gas flow. If the flame had been sheathed with an Ar flow so that air could not be entrained, the NO spectrum would be missing. Further confirmation that the observed spectrum was due to NO was obtained by adding small amounts of N_2 to the Ar nebulizer gas flow. The addition of increasing amounts of N_2 increased the observed background signals until, at fairly high N_2 flow rates (≈ 4 LPM), the signal leveled off; addition of more N_2 decreased the observed signal.

The background signal for the $H_2/O_2/Ar$ flame is higher than for the C_2H_2/air flame which has a greater source of N_2 , from the air used as an oxidant. The decrease in background ionization at high added nitrogen flow rates in the $H_2/O_2/Ar$ flame can be explained in the same way as the higher NO signal in the $H_2/O_2/Ar$ flame. The $H_2/O_2/Ar$ flame must obtain its N_2 from air entrained in its flow. But, the hydrogen flame with the low Ar flow rates used here (2 to 3

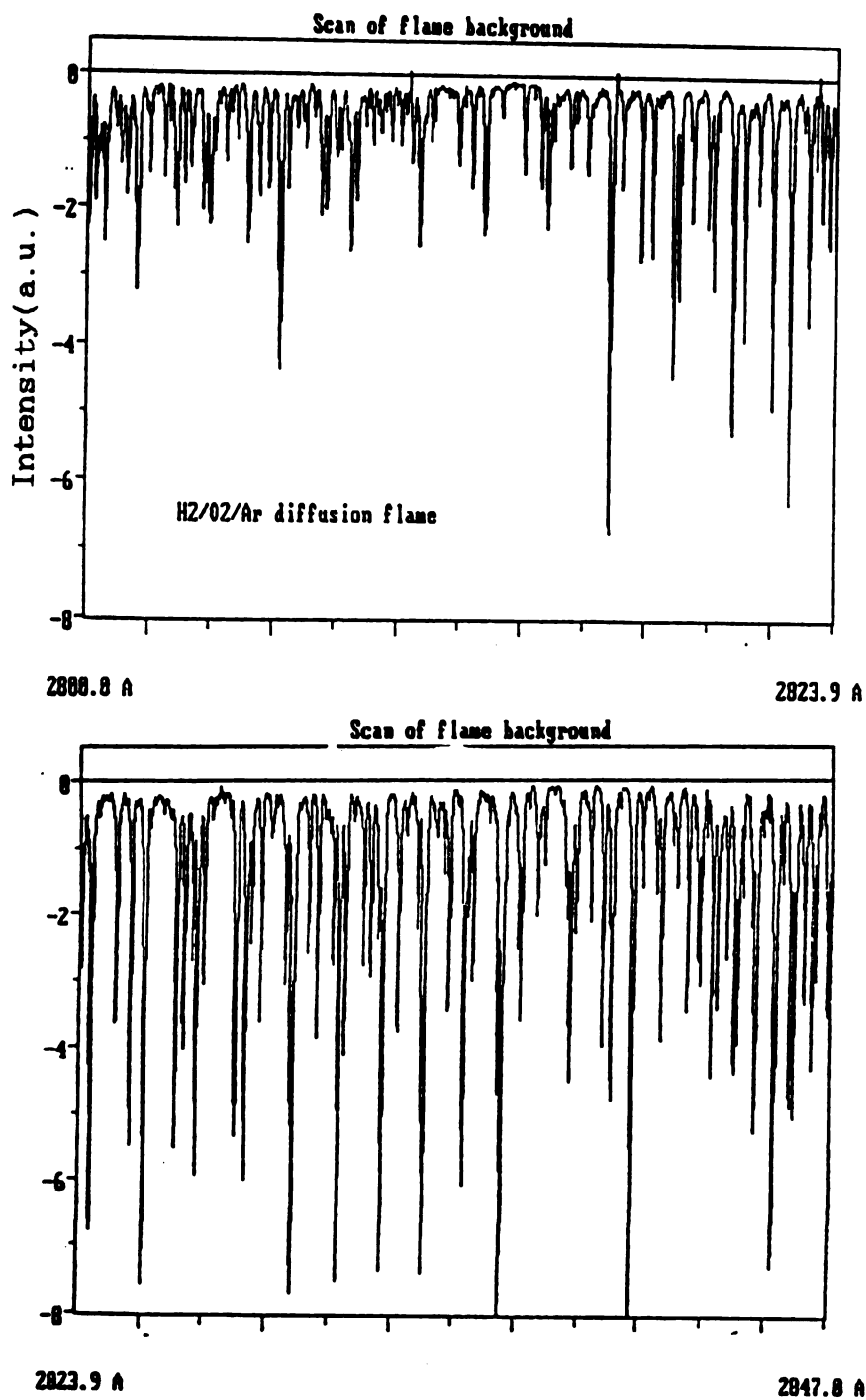


Figure 3 - 15 Background Ionization Spectrum - H₂/O₂/Ar flame.

LPM) has a temperature of ≈ 2700 K. This is 200 K higher than the acetylene flame. The formation of NO from N_2 is endothermic, and the equilibrium for the formation reaction is increased by the increased temperature. When N_2 is introduced in the hydrogen flame the amount of N_2 available for formation of NO is increased but the flame temperature is decreased. As the N_2 flow is increased the temperature effect eventually dominates. Figures 3-16 through 3-18 show the background spectra expanded to show the regions of the Mn and Na transitions probed in the experiments described in this chapter.

Structure in the background spectra is also observed in the visible region of the spectrum. In this case the laser was focused into the acetylene flame with a 10 cm focal length lens to increase the laser irradiance. The observed spectra are shown in Figure 3-19. Spectra were taken in the region of 560 nm, but no structure was observed. Background ionization was not observed with visible wavelength lasers when no focusing was used. When the laser was focused, background ionization occurred at all wavelengths probed. This may indicate that multiphoton excitations through virtual levels are causing the observed ionization. These multiphoton excitations require high irradiances to be observed.

The power dependence of the background ionization signal is also important in determining the optimum laser power to be used and whether or not a given region of the

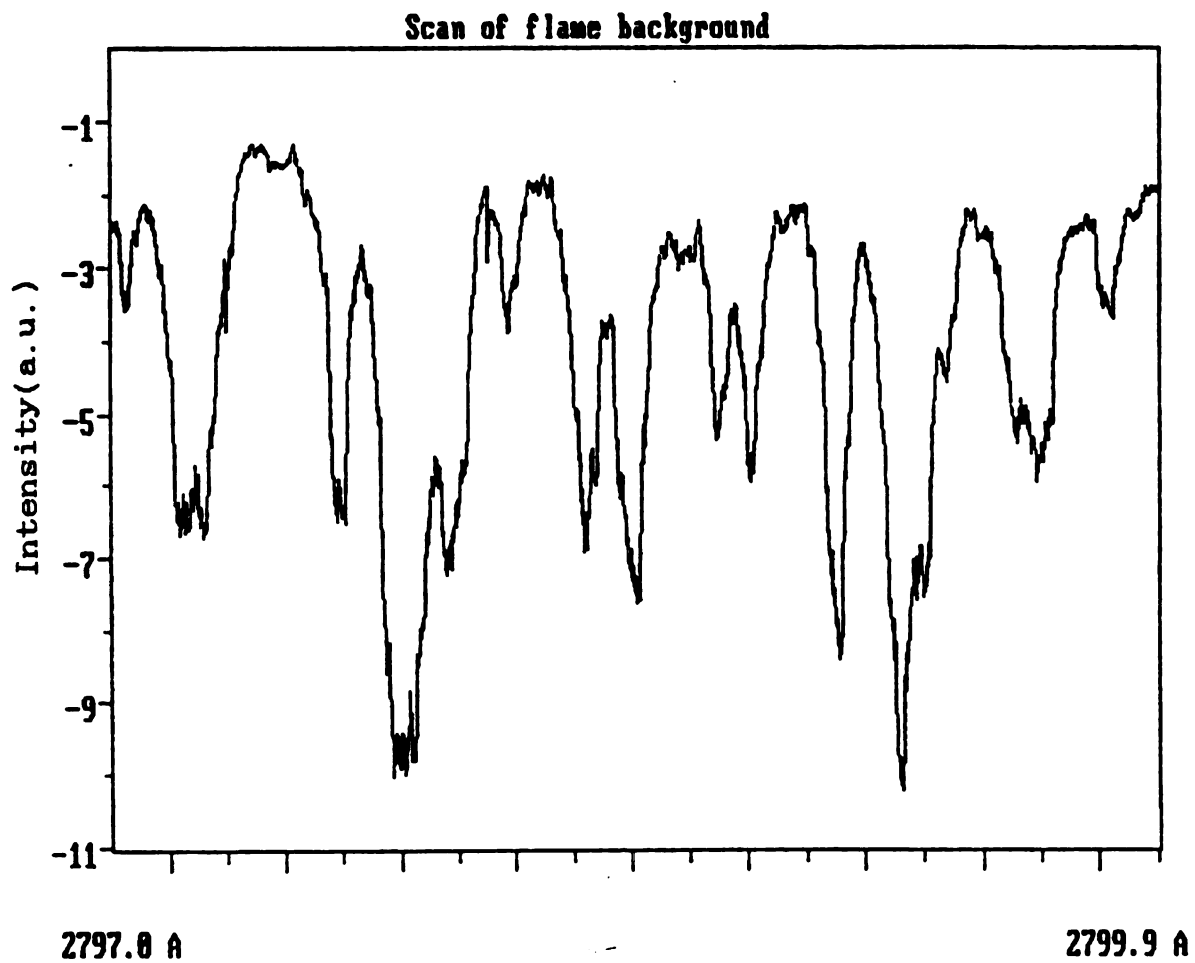


Figure 3 - 16 Background Ionization Spectrum - near the Mn transition. $\text{H}_2/\text{O}_2/\text{Ar}$ flame.

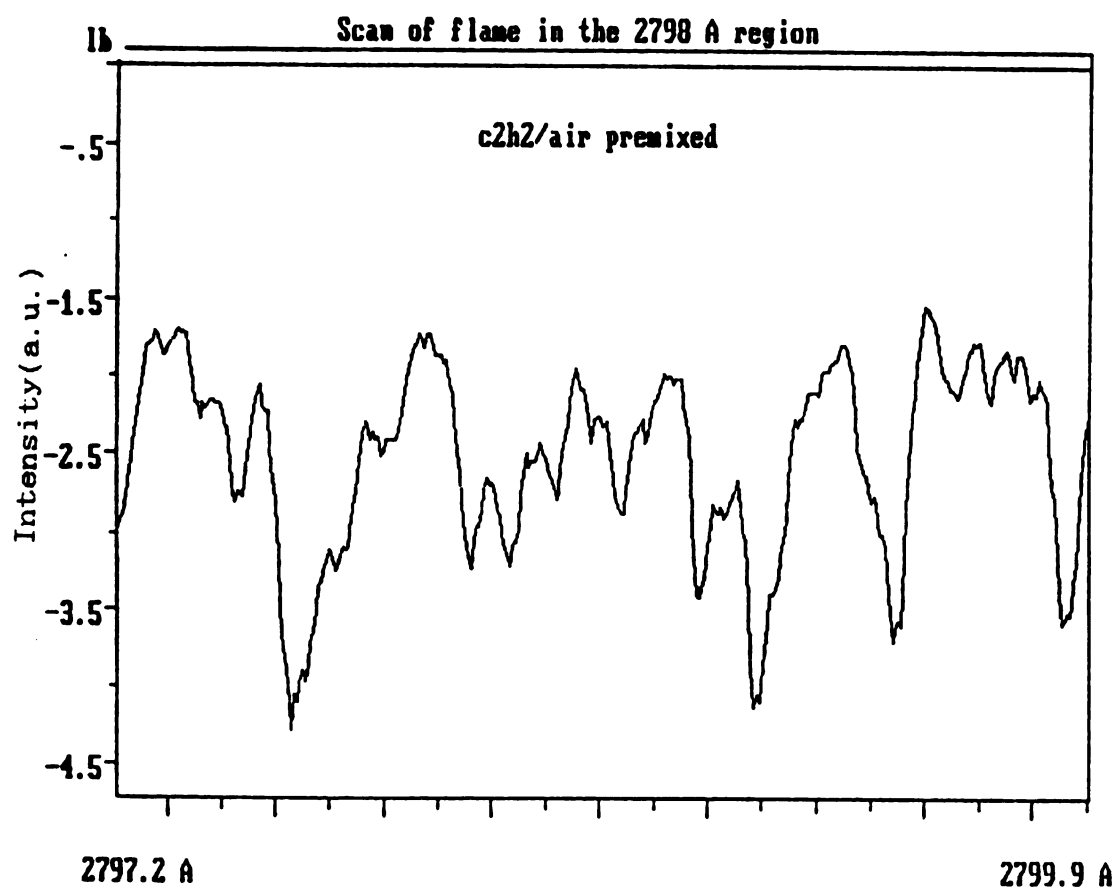


Figure 3 - 17 Background Ionization Spectrum - near the Mn transition. C_2H_2 /air flame.

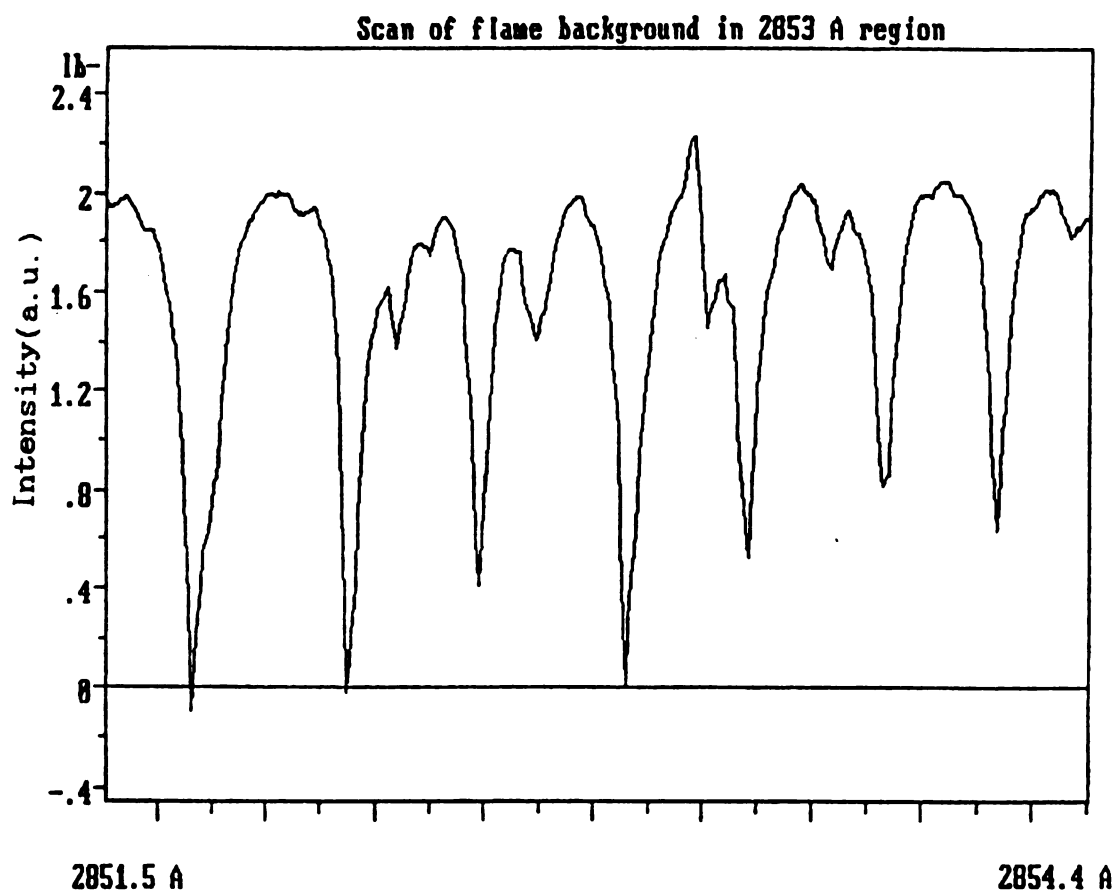


Figure 3 - 18 Background Ionization Spectrum - near the Na transition. $\text{H}_2/\text{O}_2/\text{Ar}$ flame.

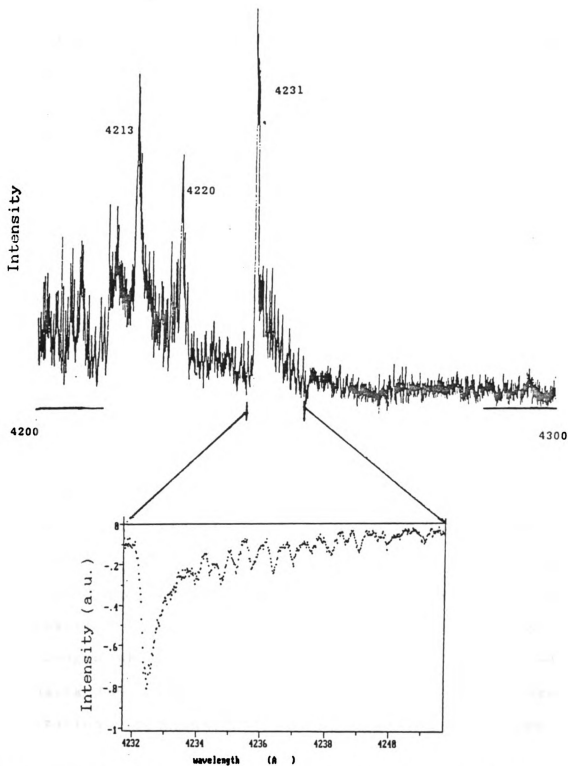


Figure 3 - 19 Background Ionization Spectrum $\text{C}_2\text{H}_2/\text{air}$ flame

wavelength spectrum will be analytically useful. Table 3-4 lists the power dependencies observed at various laser wavelengths for the acetylene flame. The laser power at 355 nm was approximately 5 times greater than at 560 nm. The power at 423 nm was approximately 4 times lower than at 560 nm and the power at 280 nm was approximately 10 times lower than at 560 nm. As expected at longer wavelengths (lower photon energies) the power dependence is higher. The higher powers and focusing sometimes used in the visible region can begin to saturate some of the multiphoton transitions observed with the background species.

Two other variables are important in minimizing background ionization of flame species. First, the composition of the flame (i.e., fuel, oxidant, diluent and fuel-to-oxidant ratio) will determine the species present to be ionized. The position of the laser beam in the flame will also determine species concentrations in the flame volume being viewed. In the acetylene flame, the composition dependence was tested at three wavelengths 280 nm, 423 nm, and 560 nm. The only wavelength where composition dependence was observed was at 423 nm. At this wavelength when the fuel to oxidant ratio was increased, changing the flame from lean to fuel rich, the background ionization increased; this indicates that perhaps the species being ionized was being formed from the acetylene. The lack of composition dependence at 280 nm was expected because NO formation would only be affected to the extent

<u>Wavelength(nm)</u>	<u>Slope</u>
280	2
355	<2 and decreasing - saturation
423	2.5 at low powers - saturation 1.2 at high powers
560	2.7 and decreasing - saturation 2.1 at high powers

Table 3 - 4 Slope of log background signal vs log relative laser power curves at various wavelengths. C_2H_2 /air flame.

that the fuel-to-oxidant ratio weakly effects the flame temperature.

The positional dependence of the background signal in the acetylene flame was also checked at the same three wavelengths. The laser beam position was changed from 1.0 cm to 1.5 cm above the burner head and the change in background ionization was observed. The background ionization at 423 nm decreased indicating that the species being ionized was perhaps an intermediate in the combustion reaction scheme which was further reacted as the combustion progressed. The background ionization at 280 and 560 nm increased as the laser beam was moved up in the flame; which indicated that the species being ionized at these wavelengths was stable and its concentration was increasing with the residence time in the flame. This is reasonable at this wavelength, where NO is being ionized. At higher positions in the flame, the N₂ would have been resident in the high-temperature flame environment for longer times, thus the higher NO signal.

Chapter IV

Comparison of Models for LII Signals

The theory of ionization spectroscopy and resonance excitation in flames has been developed primarily using rate equations (66, 100, 104) rather than the more general density matrix formalism. Photoionization theories and theories of resonance excitation have been developed using the density matrix and time-dependent perturbation theory (105, 106, 109, 111), but only infrequently has it been done with flame-based spectroscopy in mind (106). The question of whether or not the rate equations approach is accurate in the case of flame-based spectroscopy using high-powered, fast-pulsed lasers has been investigated, but only general rules for the ranges of applicability of the rate equations were given (106).

This chapter develops the theory of laser excitation and ionization spectroscopy in flames; both the density matrix and rate equations formalisms are used. The density matrix equations are developed for both single mode and multimode laser excitation. In the last section of the chapter the equations developed are used to investigate the magnitude of the errors that result from modeling resonant

laser excitation in flames with the rate equations instead of the more complicated density matrix formulation.

A. The Density Matrix Formulation for Laser Excitation in Flames

Time-dependent perturbation theory is used to develop the density matrix equations of motion for laser excitation. First, however, the concept of a density matrix is introduced. The state of an analyte particle can be written in terms of the eigenfunctions, u_n , of the Hamiltonian, H , of the particle.

$$\psi = \sum_n a_n u_n \quad (1)$$

where the values of a_n , defined by

$$a_n = \int u_n^* \psi dr \quad (2)$$

are the expansion coefficients for ψ . For an observable quantity, A , described by an operator $\hat{A}$, of the analyte the expectation value of A is

$$\begin{aligned} \langle A \rangle &= \int \psi^* \hat{A} \psi dr \\ &= \sum_m a_m^* \int u_m^* \hat{A} u_n dr a_n \text{ or} \\ \langle A \rangle &= \sum_m a_m^* A_{mn} a_n. \end{aligned} \quad (3)$$

For a system of N identical analyte particles, each with the same Hamiltonian, taking the average over the N particle of the expectation value of A yields,

$$\langle A \rangle = \sum_n \overline{a_n^* A_{nn} a_n}, \quad (4)$$

where $\overline{\quad}$ means $(1/N) \sum_{N \text{ particles}}$. Then the density matrix can be defined by

$$\rho_{nm} = a_m^* a_n \quad (5)$$

and the average above becomes

$$\langle A \rangle = \sum_n \rho_{nn} A_{nn} = \text{tr}(\rho A) \quad (6)$$

The quantity ρ_{nn} can be thought of as the probability of finding an analyte particle in the state n . Having defined the density matrix, the Schrodinger equation for interaction of a time-dependent field with the analyte can be examined.

The time-dependent Schrodinger equation is

$$\hat{H}\psi = i\hbar(\partial/\partial t)\psi(r,t) \quad (7)$$

Substituting (1) into (7) one obtains

$$\hat{H} \sum_n a_n u_n = i\hbar(\partial/\partial t) \sum_n a_n u_n \quad (8)$$

At this point, the properties of $\hat{H}$ and the a_n and u_n are examined. With time-dependent perturbation theory, $\hat{H}$ can be written as $\hat{H} = \hat{H}_0 + \hat{H}_1(t)$ and the expansion for ψ as an expansion in the eigenfunctions of the unperturbed Hamiltonian, $\hat{H}_0$. Assuming any time dependence in the Hamiltonian to be multiplicative, $a_n = a_n(t)$, $u_n = u_n(r)$ and (8) can be rewritten

$$\sum_n a_n \hat{H} u_n = i\hbar \sum_n u_n (\partial/\partial t) a_n \quad (9)$$

Multiplying by u_m^* and integrating equation (9), after some algebra, the following equation results:

$$i\hbar(\partial/\partial t) \rho_{mn} = \sum_k [H_{mk} \rho_{kn} - \rho_{mk} H_{kn}] \quad (10)$$

$$= [(H\rho)_{mn} - (\rho H)_{mn}] \quad \text{or} \quad (11)$$

$$i\hbar(\partial/\partial t) \rho = [H\rho - \rho H] = [H, \rho] \quad (12)$$

where $[A, B]$ is the commutator of A and B. The Hamiltonian can be written $H = H_0 + H_1$ and in the dipole approximation $H_1 = -\mu \cdot E(t)$, where $\mu = \int \psi_m^* e r \psi_n dr$ is the dipole moment of the transition being observed. Note that the dipole moment is zero if $m = n$. Let us assume a linearly polarized laser since experimentally, this is what is normally used, so that $\mu \cdot E$ becomes μE . If the laser is a multimode laser, the field $E(t)$ is a sum over the modes

$$E(t) = \sum_i E_i(t) \quad (13)$$

and the electric field for each mode is

$$E_i(t) = E_{0i}(t) \cos(\omega_i t) = (1/2) E_{0i} [\exp(i\omega_i t) + \exp(-i\omega_i t)] \quad (14)$$

If we substitute the resulting Hamiltonian into (12), the equations of motion for the density matrix of a two-level atomic system under laser excitation can be written as

$$(\partial/\partial t) \rho_{21} = -i\omega_0 \rho_{21} + i \sum_i (\mu_i E_i(t)/\hbar) (\rho_{11} - \rho_{22}) \quad (15)$$

$$(\partial/\partial t) \rho_{22} = -i \sum_i \mu_i E_i(t) (\rho_{21} - \rho_{12}) \quad (16)$$

where $\omega_0 = (E_2 - E_1)/\hbar$.

The effects of collisions can be taken into account in these equations phenomenologically by adding decay rates for the off-diagonal elements and the diagonal elements along with the Einstein coefficient for spontaneous emission. The ground state matrix element, ρ_{11} , has a small decay rate which will be assumed to be zero. The equations resulting from this substitution are,

$$(\partial/\partial t) \rho_{21} = -i\omega_0 \rho_{21} + i \sum_i (\mu_i E_i(t)/\hbar) (\rho_{11} - \rho_{22}) - \gamma_{21} \rho_{21} \quad (17)$$

$$(\partial/\partial t) \rho_{22} = -i \sum_i \mu_i E_i(t)/\hbar (\rho_{21} - \rho_{21}^*) - (A_{21} - \gamma_2) \rho_{22} \quad (18)$$

where $\rho_{21} = \rho_{12}^*$ has been used. Methods for calculating the terms in these equations are discussed in Section C of this

chapter. Note that the terms for collisional excitation from level one to level two have not been included. Collisional excitation occurs at a much slower rate than the rates of the other processes involved. Also, the laser pulse lengths which are used are short so that the collisional excitation contribution should not be significant in that time frame. The collisional rates are slow due to the large excitation energies involved in electronic excitations. Ion-electron recombination is also very slow and, thus, it has been neglected.

At this point the equations for a two-level atom have been developed. To model ionization experiments a two bound-level atom with an ionization continuum must be used. Figure 4-1 diagrams the energy levels and transitions involved. The ionization is treated simply as occurring at a rate which can be calculated from experimentally observed or theoretically derived collisional or photoionization cross sections. The ionization adds an extra decay out of level two which is not regained in level one. Equation (18) is changed to

$$(\partial/\partial t) \rho_{22} = -i \sum_i (\mu_i E_i / \hbar) (\rho_{21} - \rho_{21}^*) - (A_{21} + \gamma_2 + R_i) \rho_{22} \quad (19)$$

and equation (20) defines the normalization.

$$\rho_{11} + \rho_{22} + \rho_i = 1 \quad (20)$$

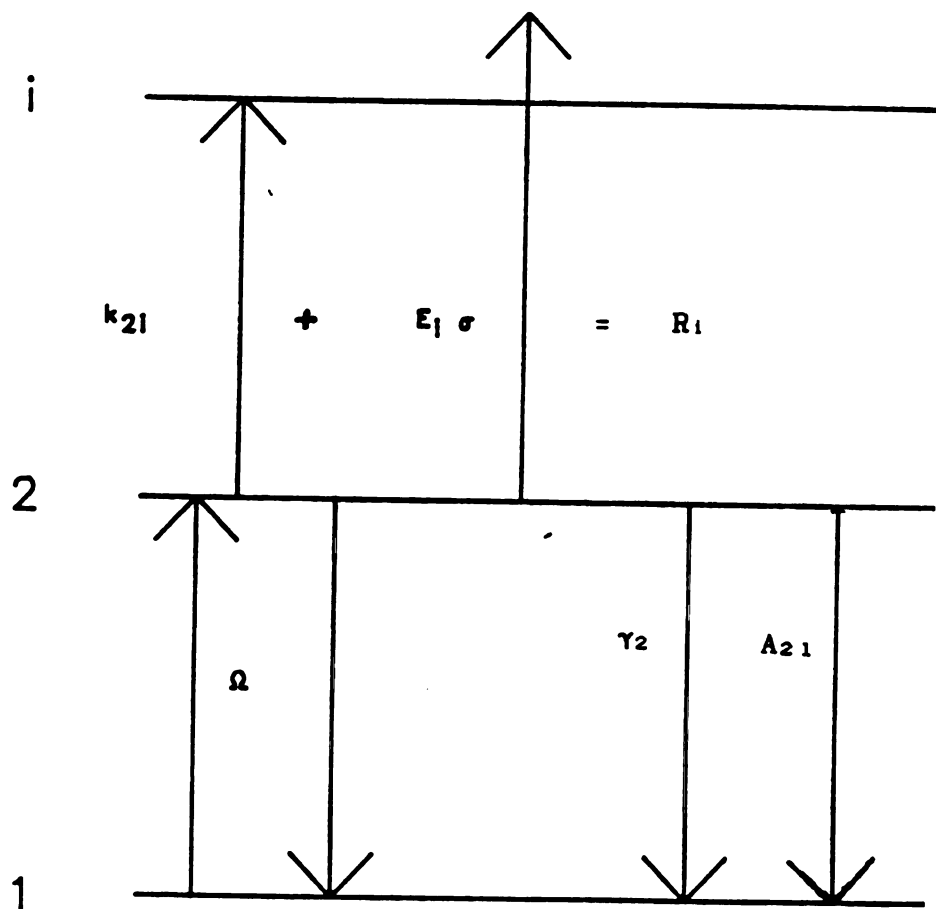


Figure 4 - 1 Transition Diagram for the Density Matrix Model

where R_1 is the total ionization rate constant, i.e., the sum of the collisional and photoionization rate constants. The quantity ρ_1 is the probability that the atom is ionized. The normalization $\rho_{11} + \rho_{22} + \rho_1 = 1$ will be used, which means that the system being considered is a two-level atom plus an ionization continuum and no other levels contribute significantly to the population transfer. There are two cases which we need to consider: 1), single-mode laser excitation and 2), multimode laser excitation. The equations for each are developed separately because the methods used to derive final expressions for the equations of motion of the density matrix in each case are quite different.

1. Single Mode Excitation

When the laser used to excite a transition in an analyte has only a single mode oscillating, the equations describing the density matrix are greatly simplified. The interaction terms drop the summation over the modes so that $\sum_i \mu_i E_i$ is now μE . If $E = (1/2)E_0[\exp(i\omega t) + \exp(-i\omega t)]$ is substituted into equation (17) the result is

$$\begin{aligned} (\partial/\partial t) \rho_{21} = & -(i\omega_0 + \gamma_{21}) \rho_{21} + i(\mu E_0/2\hbar)(\rho_{11} - \rho_{22}) \\ & \times [\exp(i\omega t) + \exp(-i\omega t)] \end{aligned} \quad (21)$$

If we define $\Omega = \mu E_0 / 2\hbar$ and $\sigma_{21} = \rho_{21} \exp(i\omega t)$, we obtain,

$$\begin{aligned} \exp(-i\omega t) (\partial/\partial t) \sigma_{21} - i\omega \exp(-i\omega t) \sigma_{21} = \\ -(i\omega_0 + \gamma_{21}) \exp(-i\omega t) \sigma_{21} + i\Omega \exp(i\omega t) [1 + \exp(-2i\omega t)] \\ \times (\rho_{11} - \rho_{22}) \end{aligned} \quad (22)$$

The quantity Ω is known as the Rabi frequency and indicates the strength of the coupling of the observed transition to the laser field. Equations (22) and the single mode equivalent of (18) can be averaged over times that are long compared to the reciprocal of the field frequency, ω^{-1} , but short compared to all other times (e.g. γ_{21}^{-1} , γ_2^{-1} , etc.). This gives

$$(\partial/\partial t) \sigma_{21} = [i(\omega - \omega_0) - \gamma_{21}] \sigma_{21} + i\Omega (\rho_{11} - \rho_{22}) \quad (23)$$

and

$$(\partial/\partial t) \rho_{22} = -i\Omega (\sigma_{21} - \sigma_{21}^*) - (A_{21} + \gamma_2 + R_i) \rho_{22} \quad (24)$$

This procedure for simplifying the density matrix equations by removing the fast time dependence is referred to as the rotating wave approximation due to its physical significance in similar equations describing nuclear magnetic resonance. The two other equations needed to solve this system are

$$(\partial/\partial t) \rho_i \approx R_i \rho_{22} \quad (25)$$

$$\rho_{11} + \rho_{22} + \rho_i = 1 \quad (26)$$

These four equations, (23)-(26), describe the time dependence of the density matrix and are used below to calculate the populations of the levels in the atomic system under single-mode, electromagnetic excitation.

2. Multimode Excitation

Single-mode, pulsed dye lasers are not commonly used in analytical spectroscopy. Therefore, in this section, equations are developed for multimode laser excitation of a two-level atomic system with ionization. This allows the validity of the rate equations to be tested under conditions that model commonly used laser systems. For example, we can model the Nd:YAG pumped dye lasers described in Chapter II which have spectral widths of $\approx 1 \text{ cm}^{-1}$. Equations (17) and (18) are the starting point for this derivation. Equations (25) and (26) are still valid, and remain unchanged, because a two-level system with ionization is assumed and the ionization rates do not depend on the mode structure of the laser.

Now let us substitute equation (14) into equations (17) and (18). If we define $\Omega = (\mu E_{10}/2\hbar)$ the result is

$$\begin{aligned}
 (\partial/\partial t) \rho_{21} = & -(i\omega_0 + \gamma_{21}) \rho_{21} - i(\rho_{22} - \rho_{11}) \sum_i \Omega_i \times \\
 & [\exp(i\omega_i t) + \exp(-i\omega_i t)] \quad (27)
 \end{aligned}$$

$$(\partial/\partial t)\rho_{22} = -i\sum_i \Omega_i [\exp(i\omega_i t) + \exp(-i\omega_i t)](\rho_{21} - \rho_{21}^*) - (A_{21} + \gamma_2 + R_1)\rho_{22} \quad (28)$$

At this point in the previous section the rotating wave approximation was applied. However, with multimode excitation, $\exp(i\omega t)$ cannot be factored from the expression for ρ_{21} , because it contains a summation over the ω_i and not a single exponential. The quantity ρ_{21} can be determined directly following the example of Daily (106) and McIlrath and Carlston (109). Making the substitution $\Delta\rho = \rho_{22} - \rho_{11}$ this procedure yields

$$\rho_{21} = -i\exp[-(i\omega_0 + \gamma_{21})t] \sum_i \int \Delta\rho \Omega_i \exp(\gamma_{21}t') \times \{\exp[i(\omega_0 + \omega_i)t'] + \exp[i(\omega_0 - \omega_i)t']\} dt' \quad (29)$$

If two assumptions are made, equation (29) can be integrated directly. The first assumption is that the Ω_i vary slowly in time compared to the convergence time for the integral, which is approximately γ_{21}^{-1} . This allows them to be removed from the integral. This is a reasonable assumption for most pulsed lasers when the probed atom is in an environment, like a flame, where energetic collisions are frequent. However, it does not hold for the very fastest pulsed lasers (i.e., those with pulse width less than 1 ns). If it is assumed that the population difference, $\Delta\rho$, varies slowly compared to the same convergence time, it may also be removed from the integral.

With these two assumptions, integration of equation (29) gives

$$\rho_{21} = -i\Delta\rho\exp[-i(\omega_0 + \gamma_{21})t] \Sigma_i \Omega_i X \quad (30)$$

where

$$X = \frac{\exp\{[\gamma_{21} + i(\omega_0 + \omega_i)]t\} - 1}{\gamma_{21} + i(\omega_0 + \omega_i)} + \frac{\exp\{[\gamma_{21} + i(\omega_0 - \omega_i)]t\} - 1}{\gamma_{21} + i(\omega_0 - \omega_i)}$$

If we define $\sigma_{21} = \rho_{21}\exp(i\omega_0 t)$ (Note that this is not the same definition used in the single mode case), the result is

$$\sigma_{21} = -i\Delta\rho \Sigma_i \Omega_i Y \quad (31)$$

where

$$Y = \frac{\exp[i(\omega_0 + \omega_i)t] - \exp(-\gamma_{21}t)}{\gamma_{21} + i(\omega_0 + \omega_i)} + \frac{\exp[i(\omega_0 - \omega_i)t] - \exp(-\gamma_{21}t)}{\gamma_{21} + i(\omega_0 - \omega_i)}$$

As in the single mode case, the optical frequency is much faster than all other rates so it is possible to average over times that are long compared to this and short compared to other times. This drops the first term and leaves

$$\sigma_{21} = -i\Delta\rho \Sigma_i \Omega_i \frac{\exp[i(\omega_0 - \omega_i)t] - \exp(-\gamma_{21}t)}{\gamma_{21} + i(\omega_0 - \omega_i)} \quad (32)$$

or

$$\sigma_{21} = -\Delta\rho \Sigma_i \Omega_i \frac{[i\gamma_{21} + (\omega_0 - \omega_i)]\{\exp[i(\omega_0 - \omega_i)t] - \exp(-\gamma_{21}t)\}}{\gamma_{21}^2 + (\omega_0 - \omega_i)^2} \quad (33)$$

If we examine only the first term in equation (28), the term dealing with the interaction of the atom with the field, the results of equation (33) and the definition of σ_{21} can be substituted into this term. The result is

$$\text{int. term} = i\Delta\rho\Sigma_{ij}W_iW_jZ \quad (34)$$

where

$$Z = \frac{[i\gamma_{21} + (\omega_0 - \omega_j)]A}{\gamma_{21}^2 + (\omega_0 - \omega_j)^2} - \frac{[-i\gamma_{21} + (\omega_0 - \omega_j)]B}{\gamma_{21}^2 + (\omega_0 - \omega_j)^2}$$

where

$$A = [\exp(i\omega_{ij}t) - \exp(i(\omega_i - \omega_0)t - \gamma_{21}t) + \exp(-i(\omega_i + \omega_j)t - \exp(-i(\omega_0 + \omega_i)t - \gamma_{21}t))]$$

and

$$B = [\exp(-i\omega_{ij}t) - \exp(i(\omega_0 + \omega_i)t - \gamma_{21}t) + \exp(i(\omega_i + \omega_j)t - \exp(i(\omega_0 + \omega_i)t - \gamma_{21}t))]$$

where $\omega_{ij} = \omega_i - \omega_j$. This can be simplified considerably again by assuming that the variation at the optical frequencies ω_0 , ω_i , and ω_j are too fast to observe. Therefore, we can average over times long compared to their reciprocals as was done previously. The result is

$$\begin{aligned} \text{int. term} = & -2\Delta\rho\sum_{i,j} \frac{\Omega_i\Omega_j}{\gamma_{21}^2 + (\omega_0 - \omega_j)^2} \times \\ & \{ \gamma_{21} [\cos\omega_j t - \exp(-\gamma_{21}t)\cos(\omega_0 - \omega_i)t] + \\ & (\omega_0 - \omega_j) [\sin\omega_j t + \exp(-\gamma_{21}t)\sin(\omega_0 - \omega_i)t] \} \end{aligned} \quad (35)$$

Recall that equation (28) can be written

$$(\partial/\partial t)\rho_{22} = \text{int. term} - (\gamma_2 + A_{21} + R_1)\rho_{22} \quad (36)$$

This can be further simplified if the phases of the modes are such that they reduce the size of the cross terms (those where $i \neq j$, with respect to the terms containing $i=j$). This is reasonable because the phases of the modes in free running pulsed dye lasers tend to be randomly fluctuating, making coherence effects between the phases insignificant. Elimination of $i \neq j$ from equation (35) gives

$$\begin{aligned} \text{int term} = & -2\Delta\rho\sum_i \frac{\Omega_i^2}{\gamma_{21}^2 + (\omega_0 - \omega_i)^2} \times \\ & \{ \gamma_{21} [1 - \exp(-\gamma_{21}t)\cos(\omega_0 - \omega_i)t] + \\ & (\omega_0 - \omega_i) \exp(-\gamma_{21}t)\sin(\omega_0 - \omega_i)t \} \end{aligned} \quad (37)$$

Now, all the equations necessary to calculate the time dependence of the density matrix elements have been developed. Equations (23) through (26) describe the motion of the atomic system under single mode laser excitation while equation (37) or (35) and (36), (25), and (26) describe multimode excitation.

B. The Rate Equations Approach

In this section the rate equations which describe the population transfer processes for a two-level atom (with ionization) under laser excitation are derived. The rate equations are a simplification of the density matrix made by assuming a steady state for the off-diagonal matrix elements, ρ_{21} and ρ_{12} . This simplification allows the description of the atomic system as only populations transferring from state to state with the field-stimulated transitions being treated as constant in time for a given laser power. Figure 4-2 diagrams the population transfer processes involved in the two level atom with ionization. The quantities B_{12} , B_{21} and A_{21} are Einstein coefficients for stimulated and spontaneous radiative transitions, U is the laser spectral irradiance, the k_{ij} are rate constants for collisional population transfers from state i to state j , K is the collisional ionization rate, and R is the photo-ionization rate. Given these processes the rate equations for this system can be written by inspection:

$$(dn_1/dt) = (k_{21} + R)n_2 - Kn_1 \quad (38)$$

$$(dn_2/dt) = B_{12}Un_1 + Kn_1 - (B_{21}U + A_{21} + k_{21} + k_{2i})n_2 \quad (39)$$

$$(dn_1/dt) = (B_{21}U + A_{21} + k_{21})n_2 - B_{12}Un_1 \quad (40)$$

$$n_1 + n_2 + n_i = 1 \quad (41)$$

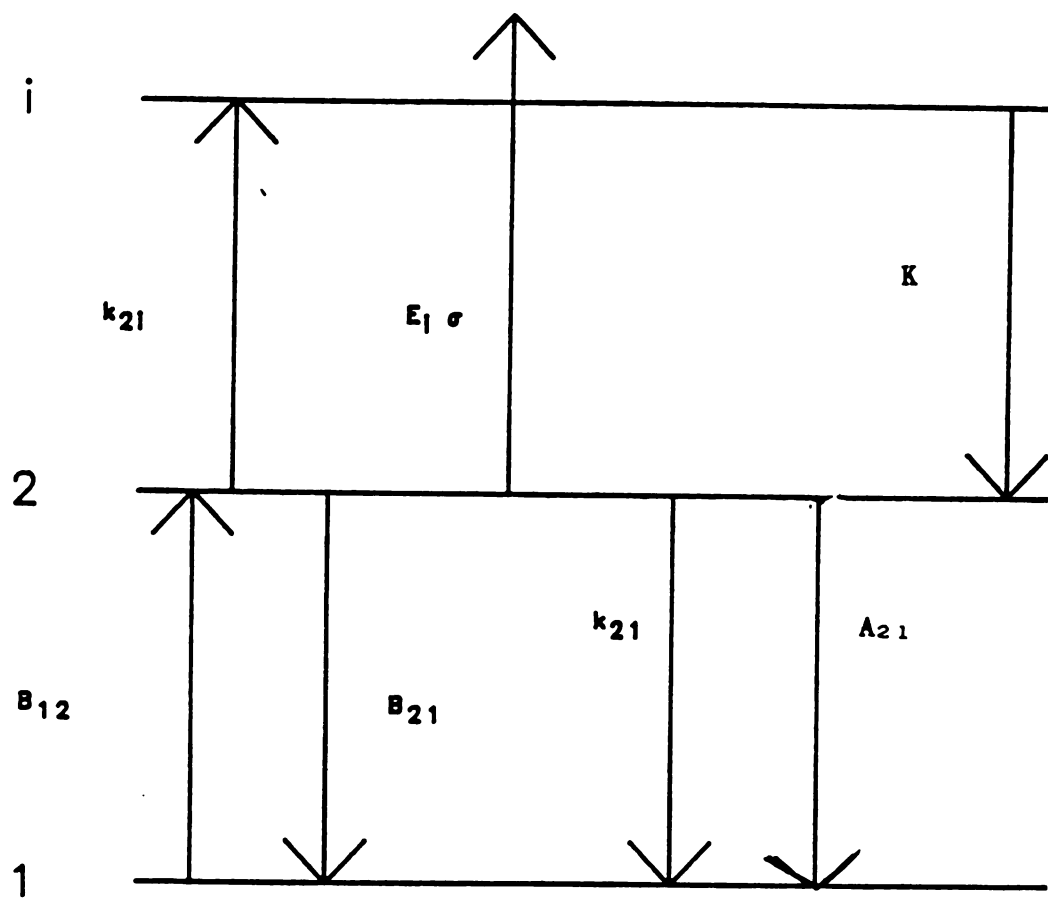


Figure 4 - 2 Transition Diagram for the Rate Equations Model

In addition to the lack of coherent interaction, there are some additional assumptions inherent in these equations.

1. The population in levels other than the three being modeled is considered to be negligible. The appearance of equation (41) in both the rate equations and the density matrix derivations shows that this assumption is inherent in both.

2. The rate constants for other processes are not disturbed by the photoionization beam if one is being used.

3. Cross sections for off-resonant multiphoton processes are small compared to those for the on-resonance and collisional processes accounted for in the model. Again, assumptions 3 and 4 are also present in the density matrix derivation of the previous section.

4. Collisional excitation may be neglected as compared to the rate of absorption of laser photons ($B_{12}U \gg$ rate of collisional excitation) as was assumed in the density matrix case. This is universally true for optical transitions with laser excitation except in the hottest environments with very low laser power irradiances.

The analytical solution of these equations has been derived by Lin (108). Full details of the solution are given in the previous reference so that only the final solutions are presented here. The solutions are:

$$n_1 = C_1 \exp(-\epsilon_1 t) + C_2 \exp(-\epsilon_2 t) + n_{1p} \quad (42)$$

$$n_2 = C_3 \exp(-\epsilon_1 t) + C_4 \exp(-\epsilon_2 t) + n_{2p} \quad (43)$$

where n_{1p} and n_{2p} are the particular solutions of equations (38) and (39) and

$$2\varepsilon_{1,2} = (K+B_{12}Ug+Z) \pm \sqrt{(K+B_{21}gU+Z)^2 - [K(K+B_{21}gU+Z) - k_{21}(K-B_{21}U)]} \quad (44)$$

At this point several symbols need to be defined:

$$g = 1 + (g_1/g_2) \quad (45)$$

where g_i is the statistical weight of state i ,

$$Z = \Lambda_{21} + k_{21} + k_{2i} \quad (46)$$

The values of C_1 , C_2 , C_3 and C_4 are related to each other by

$$C_3 = C_1(K - \varepsilon_1)/k_{2i} \quad \text{and} \quad C_4 = C_2(K - \varepsilon_2)/k_{2i} \quad (47)$$

C_1 and C_2 are obtained from the boundary conditions at $t = 0$ $n_i(0) = n_{i0}$ and $n_2(0) = n_{20}$ where n_{i0} and n_{20} are obtained by solving the equations in steady state without laser irradiance. The solution for C_1 and C_2 yields

$$C_1 = \frac{X(K - \varepsilon_2)}{(\varepsilon_1 - \varepsilon_2)} - \frac{Yk_{2i}}{(\varepsilon_1 - \varepsilon_2)} \quad (48)$$

$$C_2 = \frac{Yk_{2i}}{(\varepsilon_1 - \varepsilon_2)} - \frac{X(K - \varepsilon_1)}{(\varepsilon_1 - \varepsilon_2)} \quad (49)$$

where

$$X = n_{10} - n_{1p} \quad \text{and} \quad Y = n_{20} - n_{2p} \quad (50)$$

The particular solutions of (38) and (39) are

$$n_{1p} = B_{12} U k_{21} / \epsilon_1 \epsilon_2 \quad \text{and} \quad n_{2p} = B_{12} U K / \epsilon_1 \epsilon_2 \quad (51)$$

These equations and those of the previous sections allow the calculation of the population in any of the three levels of interest at any time after the start of the laser pulse. Whether one set of equations is valid depends on the parameters of the experiment. In Section D the effect of experimental parameters on the difference in calculated results for the different sets of equations is presented.

C. Calculation of Parameters

The equations derived in the previous two sections contain a number of parameters which must be calculated. Some of the parameters from the density matrix equations can be related to those in the rate equations. For example, the quantity γ_2 is equal to k_{21} , the collisional decay rate for the excited state. Also, $n_1 = \rho_{11}$, $n_2 = \rho_{22}$, and $n_i = \rho_{ii}$. These are the populations of the various levels. Finally,

$R_i = k_{21} + R$. Thus, the total ionization rate is the sum of the collisional and photoionization rates.

1. Collision-Induced Rates

There are three types of collision-induced processes involved in these equations, collisional deexcitation of the excited state, collisional ionization of the excited state, and collisional dephasing of the radiation-induced dipole (the off-diagonal density matrix elements).

Collisional deexcitation rates can be calculated from cross sections as can collisional dephasing rates if cross sections are available or can be measured (107).

The equation which describes this calculation is

$$\gamma \text{ or } k = \sum_p n_p v_{ip} \sigma_p \quad (52)$$

where n_p is the number density of the collision partner, and v_{ip} is the relative velocity, which is given by,

$$v_{ip} = (8k_b t / \pi \mu_{ip})^{1/2} \quad (53)$$

In equation (53) k_b is Boltzmann's constant, μ_{ip} is the reduced mass for the collision pair and σ_p is the cross section for the collision-induced process. Alternately, the collisional deexcitation rate can be calculated from the excited state lifetime with the aid of

$$\tau_i = (\gamma_i + A_{i1})^{-1} \quad (54)$$

Collisional deexcitation cross sections have been measured for a number of atomic and molecular species found in flames. Thus, the necessary data for this calculation is available. Table 4-1 shows the results of the calculation of the deexcitation rate constant for sodium in the $^2P_{1/2,3/2}$ excited state. Cross sections were taken from a tabulation compiled by Daily (107).

The decay rate for the off-diagonal density matrix element is the sum of two parts. One part is the dephasing due to elastic collisions and the other is dephasing due to inelastic collisions (i.e., the deexcitation collisions. The equation is $\gamma_{21} = (1/2)\gamma_2 + \gamma_{\text{elast}}$). The elastic part can be calculated from cross sections for elastic collisions.

The total dephasing rate can also be calculated in the following manner. In the steady-state limit for the populations ρ_{22} and ρ_{11} , and for the off diagonal element ρ_{21} , the excitation or emission profile can be calculated from the frequency dependence of the interaction term in equation (24). The result is a Lorentzian function of the form $\gamma_{21}/[\gamma_{21}^2 + (\omega - \omega_0)^2]$, so that the excitation profile directly gives the value for γ_{21} . However, in the flame, the atoms and molecules are at high temperature so that they have a fairly high speed. This gives rise to a Doppler broadening which complicates the above profile. Doppler broadening yields a Gaussian distribution so the resulting

<u>Collision Partner</u>	<u>Cross Section($\text{\AA}^2$)</u>	<u>$k_{21}(\gamma_2)(\text{s}^{-1})^*$</u>	<u>$k_{21}(\gamma_2)(\text{s}^{-1})^\#$</u>
Ar	1.9	1.2×10^8	1.1×10^8
N ₂	21	1.1×10^9	1.0×10^9
H ₂ O	2.2	1.5×10^8	1.4×10^8
CO	41	2.8×10^9	2.5×10^9

Table 4 - 1 Collisional deexcitation rate constants for Sodium in the $^3P_{1/2,3/2}$ state. * - T=2000 K, # - T=2500 K.

line profile is a convolution of the Lorentzian and Gaussian profiles, which is called a Voigt profile. In order to retrieve γ_{21} , the line profile must be deconvoluted into its parts. From the overall profile the a-parameter is calculated. The a-parameter describes the relative widths of the Doppler and Lorentzian profiles

$$a = (\Delta\nu_L / \Delta\nu_D)(\ln 2)^{1/2} \quad (55)$$

where $\Delta\nu_D$ and $\Delta\nu_L$ are the line widths (FWHM) of the Doppler and Lorentz functions. The Doppler profile can be calculated from theory if the temperature of the gas is known. The Doppler width is given by

$$\Delta\nu_D = \nu_0 (8kT \ln 2 / mc^2)^{1/2}. \quad (56)$$

From equations (55) and (56) and the measured or known value of the a-parameter, the value of $\Delta\nu_L$ can be calculated. Then γ_{21} can be derived from this by noting that the Lorentzian profile described above has a width given by $\Delta\nu_L = \gamma_{21} / \pi$. These a-parameters have been measured for many metals in many types of flames and Alkemade et al. (110) have tabulated a number of them. Table 4-2 shows several values of γ_{21} calculated from these measured profiles.

The collisional ionization rate constant k_{21} can be calculated from an expression similar to equation (52)

<u>Element</u>	<u>λ (Å)</u>	<u>Flame</u>	<u>Temp(K)</u>	<u>a</u>	<u>γ_{21} (s⁻¹)</u>
Na	5890	C ₂ H ₂ /air	2500	0.71	1.0x10 ¹⁰
		C ₂ H ₂ /O ₂ /Ar	2493	0.77-0.88	1.1-1.3x10 ¹⁰
		city gas/air	2080	1.0	1.3x10 ¹⁰
		CO/air	1964	0.45	5.7x10 ⁹
Zn	3075.9	C ₂ H ₂ /O ₂ /N ₂	2300	1.93	3.1x10 ¹⁰
Ca	4227	C ₂ H ₂ /air	2450	0.66-0.84	9.9x10 ⁹ -1.3x10 ¹⁰
Li	6708	C ₂ H ₂ /air	2500	0.55	1.4x10 ¹⁰
		H ₂ /O ₂ /N ₂	2000	0.30	6.6x10 ⁹
Al	3944	C ₂ H ₂ /N ₂ O	3000	0.81	1.8x10 ¹⁰

Table 4 - 2 Off-diagonal density matrix element's decay rate constants calculated from a-parameters

modified by $\exp(-(E_1-E_2)/kT)$ (E_1 is the ionization energy of the analyte and E_2 is the excited state energy (112)). The cross sections in the expression would then be the collisional ionization cross section for the analyte in the pumped excited state, which may be found in the literature (110). The typical value of the collisional ionization cross section for alkali metals in N_2 diluted flames is $\approx 10^{-16} \text{ cm}^2$, which gives a value of k_{21} between 10^4 and 10^8 for excited state-to-ionization continuum energies in the range of 1 to 3 eV and at typical analytical flame temperatures.

Collisional excitation from the ground state to the pumped state was neglected in both cases: however, if it were included, the value of k_{12} can be determined by assuming a Boltzmann distribution between the ground and excited states without laser excitation as long as the value of k_{21} (γ_2) is known.

2. Atom-field Interactions

There are two atom-field interactions which must be considered; first the pumping of the ground-to-excited state transition and secondly the photoionization of the excited atom. As mentioned in Section A, the photoionization process can be treated as a rate process. The photoionization rate constant, R , can be calculated with (113),

$$R = \sigma \phi, \quad (57)$$

where σ is the photoionization cross section from the excited state, which is a function of the wavelength of the ionization laser, and ϕ is the photon flux in photons/cm²s.

Photoionization cross sections for atoms in excited states have been calculated by many groups (114-116). The photoionization cross section drops off slowly with increasing energy above the ionization threshold. Also, the photoionization cross section at threshold increases as the energy of the excited state approaches the ionization energy (i.e., the photoionization cross sections for Rydberg states are greater than those for lower energy excited states). However, because collisional ionization of Rydberg levels is very efficient in flames it will generally dominate the photoionization term unless very high laser power densities are used.

For lower energy excited states (principal quantum number less than 10), the values of the photoionization cross section lie in the range of 0.1 to 100 Mb (1Mb=10⁻¹⁸ cm²). Photon fluxes can be calculated from the laser irradiance and wavelength. Typically a photoionization rate of 10⁸ s⁻¹ can be achieved with a well-matched wavelength and sufficient laser power, although it is possible to conceive of rates approaching 10⁹ s⁻¹ in the best cases. The upper limit on the photoionization rate is set by the highest laser power density which can practically be used without causing significant background photoionization.

In the case of the rate equations, the magnitude of the atom field interaction for the bound-bound transition is given by the product of the Einstein coefficients for stimulated absorption and emission and the laser spectral irradiance, $B_{12}U$ and $B_{21}U$. These are the rate constants for absorption and stimulated emission, respectively. The coefficient B_{21} can be calculated from the Einstein coefficient for spontaneous emission, A_{21} , by

$$B_{21} = A_{21}(c^2/2h\nu_{21}^3) \quad (58)$$

where $\nu_{21} = (E_2 - E_1)/h$. The Einstein coefficients are tabulated for many atomic transitions (117). The coefficient B_{12} is related to B_{21} by the ratio of the statistical weights $B_{12}g_1 = B_{21}g_2$.

For the density matrix, the atom-field interaction for the bound-bound transition is described by the Rabi frequency which was defined in Section A.1. To calculate the Rabi frequency the dipole moment of the transition and the magnitude of the electric field of the laser must be found. The electric field can be calculated from the irradiance of the laser (power per unit area irradiated) by

$$E = (P/\epsilon_0 c A)^{1/2} \quad (59)$$

The dipole moment of the transition can be calculated from the Einstein coefficient for spontaneous emission by

$$\mu_{ij} = (3h\epsilon_0 \lambda^3 A_{ij} / 64\pi^3)^{1/2} \quad (60)$$

where ϵ_0 is the permittivity of free space and all units are in the SI system. Table 4-3 shows the values of B_{12} and Ω calculated for the sodium D lines. This is an example of a transition with a large dipole moment and a transition with a dipole which is an order of magnitude less (i.e., a weak transition). The value of Ω is calculated for two different laser irradiances so that calculations of the time dependence of the populations could be made under a variety of conditions.

3. Calculation of Ion-Electron Recombination Rates

The ion-electron recombination reaction is a second order process. Thus, to calculate a first order rate constant, K , for the recombination reaction, the electron density must be known. The useful relationship is $K = k_r n_e$, where k_r is the second order rate constant and n_e is the electron number density. The electrons in the area of the ions formed by the laser come from three different sources: 1) ions formed from the flame gases during combustion; 2) ions formed from low ionization potential elements aspirated into the flame with the sample; and 3) ions formed by the laser pulse. Which of the three dominates is a function of the type of flame, its temperature, and the type and

$A_{21} \text{ (s}^{-1}\text{)}$	$B_{12} \text{ (cm}^2\text{HzW}^{-1}\text{s}^{-1}\text{)}$	$\Omega \text{ (s}^{-1}\text{)}^*$	$\Omega \text{ (s}^{-1}\text{)}^\#$
6.28×10^7	6.46×10^{17}	9.83×10^{10}	9.83×10^9
6.28×10^5	6.46×10^{15}	9.83×10^9	9.83×10^8

Table 4 - 3 Einstein coefficients and Rabi frequencies calculated from the Einstein coefficient for spontaneous emission. * - $I=1\text{MW/cm}^2$, # - $I=10\text{kW/cm}^2$.

concentrations of species in the sample as well as the laser powers and wavelengths used. In the density matrix calculation the value of K was assumed to be small enough to be negligible. To show that this is reasonable, an upper limit on K (i.e., n_e^-) is calculated below with data available from the literature.

The value of k_r in several atmospheric pressure flames has been tabulated by Alkemade et al.(110) and is in the range of 10^{-7} to 10^{-9} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The nascent electron concentration in the flame is calculated assuming that the concentration of positive ions is equal to the concentration of electrons (i.e., the number of negative ions is less than the number of electrons (118)).

In hydrocarbon flames the highest ion concentration is at the top of the primary combustion zone. The value may be as high as 10^{12} cm^{-3} , but it decays very rapidly above that point. Thermal ionization of low ionization energy elements introduced with the sample matrix requires a little more calculation. The concentration in the sample must be multiplied by a dilution factor which is a function of flame gas flow rates and sample uptake rate. With typical values of the dilution factor, no more than 10^{13} cm^{-3} electrons should be formed at reasonable concentrations (<1000 ppm) of low ionization potential elements (Cs was used as an example for the calculations) in high temperature flames (>2500 K). The number of ions formed by the LII of the analyte will be less than this because the LII technique is applied to low

analyte concentration samples. If 10^{13} cm^{-3} is taken as the highest possible value of the electron concentration and a value of $k_r = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ is used, the resulting value of K is 10^4 s^{-1} (upper bound). This is smaller than any other rate yet calculated by several orders of magnitude. Also, because fast pulsed lasers ($\approx 10 \text{ ns}$) are used for this work only $\approx 10^{-2} \%$ of the ions formed should recombine in the length of time that the lasers are forming ions. Therefore, it can be considered reasonable to neglect recombination in the density matrix calculations.

4. Characteristics of Commonly Used Dye Lasers

The characteristics of commonly used dye lasers are shown in Table 4-4. These can be used to calculate laser power densities and give reasonable pulse times to use in calculations. The spectral characteristics of commercial pulsed dye lasers are similar owing to their similar designs (i.e., oscillator cavities with gratings used in high ($\sim 5\text{th}$) order for wavelength discrimination followed by amplifier cells (usually one or two) for increasing peak powers). Typically, spectral widths of approximately 1 cm^{-1} at 560 nm are achieved in most commercial systems. Widths of 0.05 cm^{-1} are available with optional etalons in the oscillator cavity used for additional narrowing. For the multimode density matrix calculations a Gaussian laser emission spectrum is assumed and the spectral widths of

<u>Pump Laser</u>	<u>Pulse Length(ns)</u>	<u>Peak Power(MW)</u>	<u>Peak Power (freq. doubled)</u>
Nd:YAG	5 to 7	1 to 10	up to 1
N ₂	1 to 3	0.005 to 0.1	up to 0.005
excimer	~ 25	~ 1	up to 0.1
copper vapor	~ 30	up to 0.02	up to 0.001
flashlamp	100 to 1000	~ 0.01	

Table 4 - 4 Typical Characteristics of Commercial Dye
Lasers Commonly Used for Laser Ionization and Fluorescence

1cm^{-1} and 0.05cm^{-1} are used to calculate the number of modes and the power in each mode. For the 1 cm^{-1} spectrum, 75 modes are used, which cover the laser spectrum to 0.3 of its peak value on either side of the maximum and consume 90% of the integrated area. For the narrowed laser (0.05 cm^{-1}), 11 modes are used, which covered the laser spectrum to 0.25 of its peak value on either side of the maximum. In terms of the total power, a high power of 1 MW/cm^2 was chosen, which corresponds to one of the high powered lasers unfocused or one of the lower powered lasers focused in the flame. A low power of 10 kW/cm^2 corresponds to one of the lower powered lasers unfocused. These are total powers, integrated over the laser spectrum.

D. Results of Calculations

In this section the results of calculations made with the equations derived above are presented. The equations are used to calculate the error associated with modeling LII signals with rate equations, the most common approach, instead of the more general density matrix model. The calculations are performed with parameters which describe a variety of experimental conditions typically found in LII experiments. The results are also applicable to laser induced fluorescence (LIF) experiments when the fluorescence is integrated over the laser pulse. However, the results are not generally applicable to fluorescence lifetime

measurements. The LII model can be assumed to describe LIF signals because the ionization rate can be assumed constant over the laser pulse. Therefore, the total ionization is an integration of the excited state population over the laser pulse.

The first calculations are to validate the assumption that the recombination rate is negligible by varying the value of K in the rate equations and observing the effect or rather the lack of effect. Second, the error in using rate equations for highly saturated transitions is studied. Then, the error for weaker transitions (transitions with lower dipole moments) is studied for high and low laser powers (irradiances). Last, the effect of varying quenching rates and dephasing rates on the different models is studied.

The initial values of all the parameters for both models are listed in Table 4-5. The purpose of Chapter IV is to analyze the errors associated with using simplified models, the rate equations, to describe LII and LIF experiments. To this end parameters describing typical experimental conditions have been chosen.

The initial case is Na in a $H_2/O_2/Ar$ flame. This is a useful starting point because the constants are well known. The choice of ionization rate is somewhat arbitrary since it is treated a rate constant so that it does not change the coupling of the bound states. The rate chosen is reasonable for an ionization experiment. It is also unimportant to the

Density Matrix Parameters		Rate Equations Parameters	
γ_2	$1.2 \times 10^8 \text{ s}^{-1}$	=	k_{21}
A_{21}	$6.28 \times 10^7 \text{ s}^{-1}$	=	A_{21}
γ_{21}	$1.0 \times 10^{10} \text{ s}^{-1}$		$B_{12} \quad 6.46 \times 10^{17} \text{ s}^{-1} \text{ W}^{-1} \text{ cm}^2 \text{ Hz}$
irradiance	1 MW/cm^2		$U \quad 3 \times 10^{-5} \text{ W/cm}^2 \text{ Hz } (\Delta\nu = 1 \text{ cm}^{-1})$
R_i	$1 \times 10^8 \text{ s}^{-1} = k_{21} + R$		$k_{21} \quad 1.4 \times 10^4 \text{ s}^{-1}$
			$R \quad 1 \times 10^8 \text{ s}^{-1}$
			$K \quad 1 \times 10^4 \text{ s}^{-1}$

Table 4 - 5 Initial Values of Parameters for Calculations
The parameters describe Na D-lines in a $\text{H}_2/\text{O}_2/\text{Ar}$ flame environment.

calculations whether the ionization is by photons or by collisions, since both are treated as rates of population removal from the excited state. The initial case serves as a treatment of highly saturated phenomena, a frequently encountered condition with high-powered, pulsed lasers.

After the initial case is calculated, the parameters are varied to describe weaker transitions, lower laser powers and commonly used flames with higher quenching rates than the $\text{H}_2/\text{O}_2/\text{Ar}$ flame. It is not the purpose of this chapter to describe specific transitions, but rather to present a description of the errors inherent in simplified models for a wide range of commonly encountered experimental conditions in flame LII and LIF experiments. Therefore, the exact values of the parameters are not as important as their approximate values in terms of the general experimental conditions they describe and the sensitivity of the resulting calculations to the parameters' values.

1. The Negligibility of Recombination

In Section C of this chapter the upper limit for the recombination rate constant K , was calculated to be 10^4 s^{-1} . To test whether K is indeed negligible, the rate equation model was used to calculate the ion and excited state populations as a function of time for $K=10^4$ and 10^3 s^{-1} . The results of the two calculations are not shown because the effect of K was less than $10^{-4}\%$ for all times during the

laser pulse. The result was predicted from the value of K and the duration of the laser pulse, but the calculation was performed for the purpose of verification.

2. Highly Saturated Transitions, Na D-lines at High Laser Powers

The initial case to be calculated describes Na in a $H_2/O_2/Ar$ flame at 2000 K. This is a good starting point because the parameters for the calculations were easy to find or calculate. This is also the flame used by Lin (108) and the base condition he used in his models using the rate equations. There are two ways in which the rate equations can fail to model the population motion of the atomic system correctly. First, the rate model will not indicate any coherence in the systems response if it exists. Secondly, even if no coherence exists, the rate equations can give incorrect values for the population motion during the laser pulse.

In the density matrix calculations three different spectral widths of the laser were used. Either the laser is a single mode laser so that all of the power is contained in a narrow band of frequencies, or the laser is multimode, where the number of modes that oscillate is determined by the spectral width. Two spectral widths are used for the multimode cases. One describes a typical pulsed dye laser with a grating used for the wavelength selection. The other

describes a similar laser with an etalon used for spectral narrowing. Single-mode, pulsed lasers are not common, although it is possible to pulse-amplify a single-mode laser. The single-mode case is included here for completeness.

Multimode lasers reduce the coherence of the system because of a reduction in the coherence of the laser field due to the multiple modes oscillating. For most pulsed lasers coherent effects cannot be observed because of the incoherence of the laser output. When single-mode lasers are used, the field is coherent; therefore, the system response may also be coherent. Figure 4-3 shows the coherence in the Na-flame system response to a single-mode excitation. The pulsations in the excited state population at the Rabi frequency are a result of the coherence in the system response. Note the short time scale (0.5 ns full scale) used in Figure 4-3 to show the pulsations at the fast Rabi frequency. The smooth line under the density matrix result is the rate equations result. The rate equations cannot describe coherent phenomena as a result of the approximations used in deriving them. The errors in predicted ionization signals or integrated fluorescence signals due to the use of the simpler rate equations for the system shown in Figure 4-3 are shown in Figure 4-4. The errors for these type of measurements are small, 3.4% for a 1 ns laser pulse, 1.4% for a 3 ns laser pulse and <1% for a 5 ns laser pulse. The errors decrease with longer pulses as

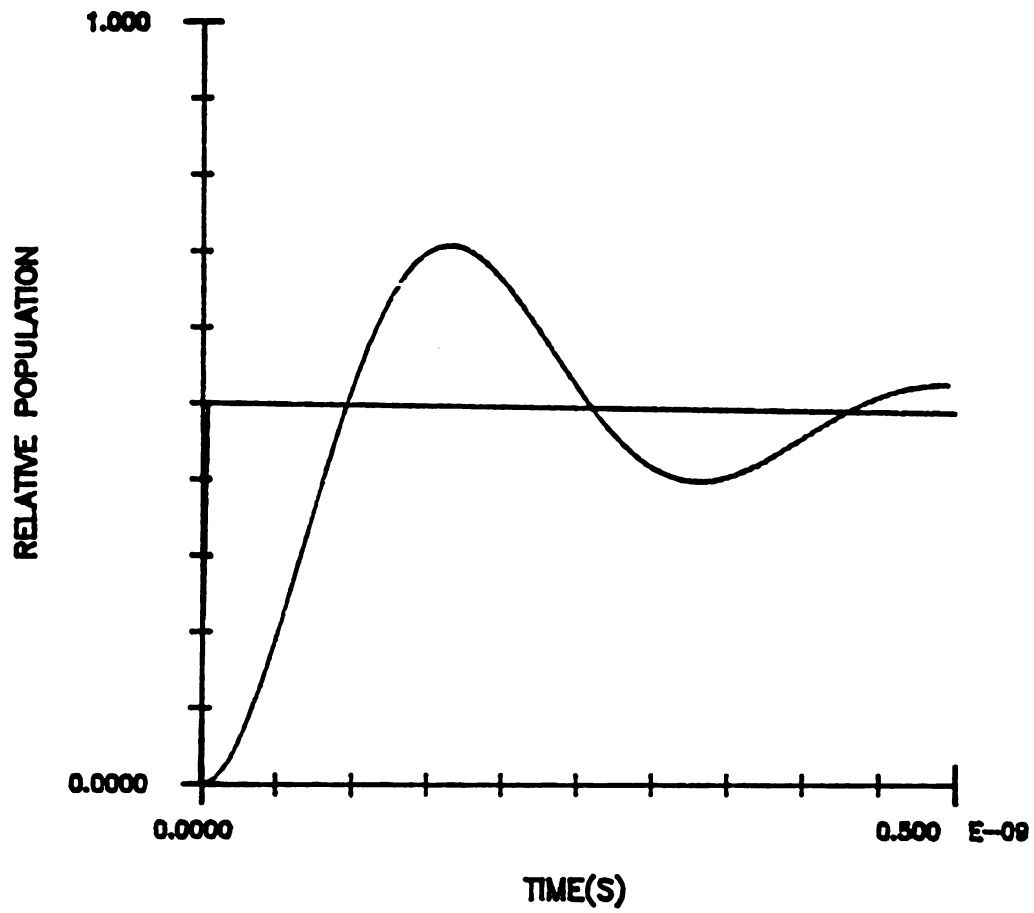


Figure 4 - 3 Comparison of Results for Single Mode Excitation. Laser irradiance 10 kW cm^{-2} .

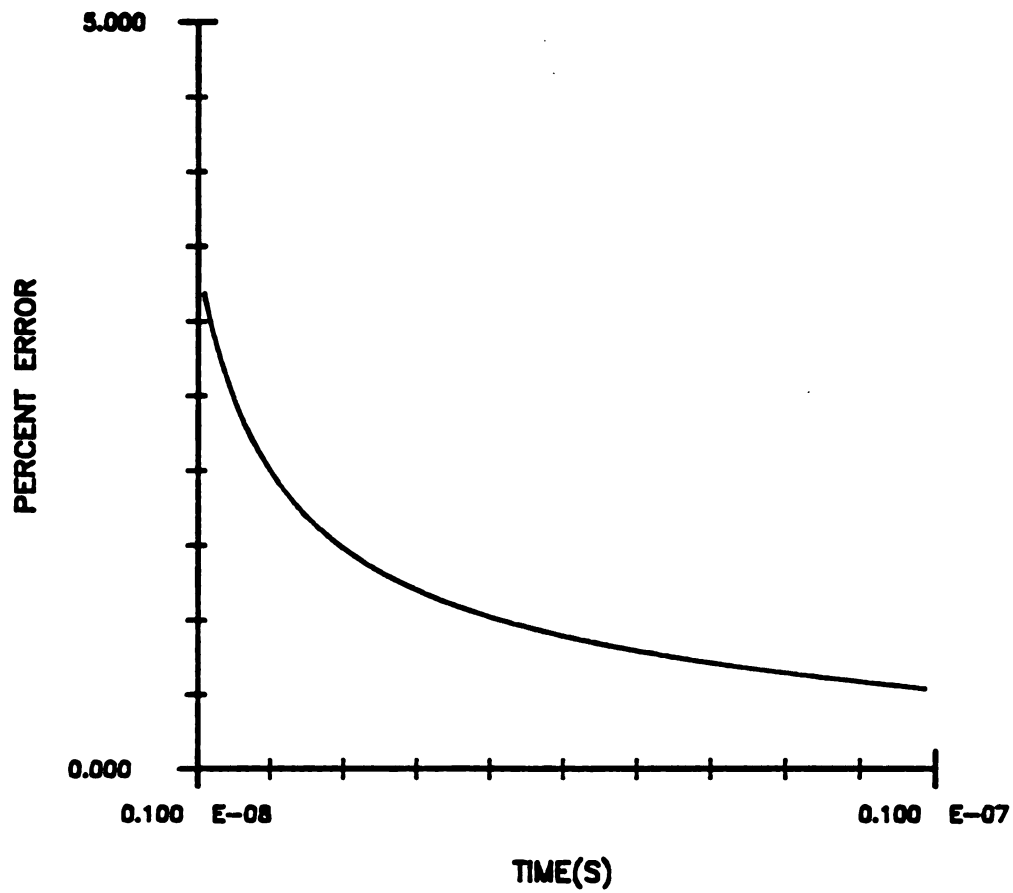


Figure 4 - 4 Error in Rate Model for Single Mode Excitation

the pulsations about the mean average together and are damped by dephasing in the flame environment. For times shorter than 1 ns, the errors become much larger but shorter width pulses are not commonly used in analytical measurements.

Because single-mode, pulsed lasers are not commonly used, the rest of the error calculations are done with the multimode laser excitation model. The multimode model is descriptive of the laser system used in the experiments described previously. Figure 4-5 shows the results of calculation of the excited state population for the initial system of Table 4-5 for a laser with a spectral width of 1 cm^{-1} . The time scale is expanded to show the beginning of the laser pulse more clearly. There is no pulsation in the density matrix result because there is little coherence in the field given the large number of modes. Also, the laser power is spread into the large number of modes, which makes the Rabi frequency for each mode much smaller allowing any coherence to be dephased. The rate equations saturate earlier in the pulse than the density matrix model; therefore, they predict a higher ionization or integrated fluorescence signal. However, for this case where the transition saturates early in the pulse, even for the density matrix result, the errors for typically used pulse widths are small.

For a 5 ns pulse Figure 4-6 shows the error in a predicted signal would be 5.6%. For shorter pulses the

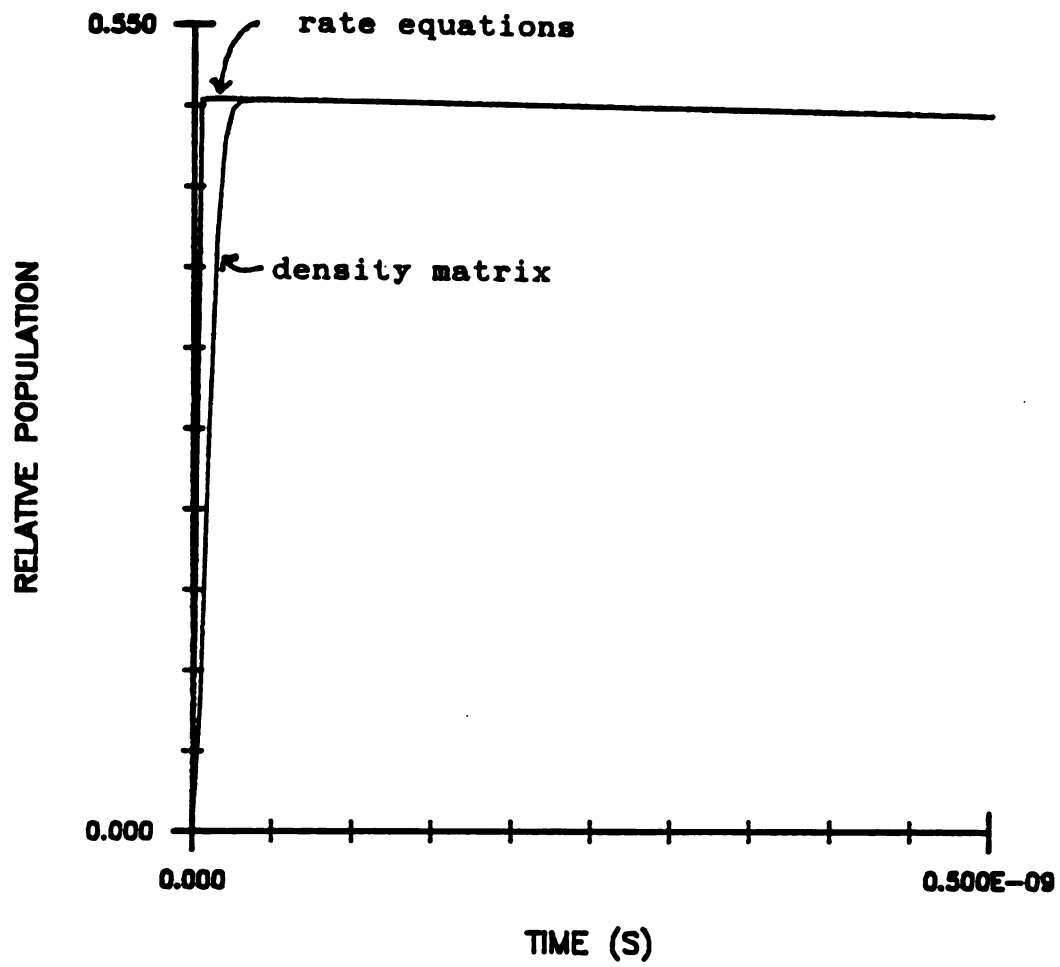


Figure 4 - 5 Comparison of Results for Multimode Excitation.

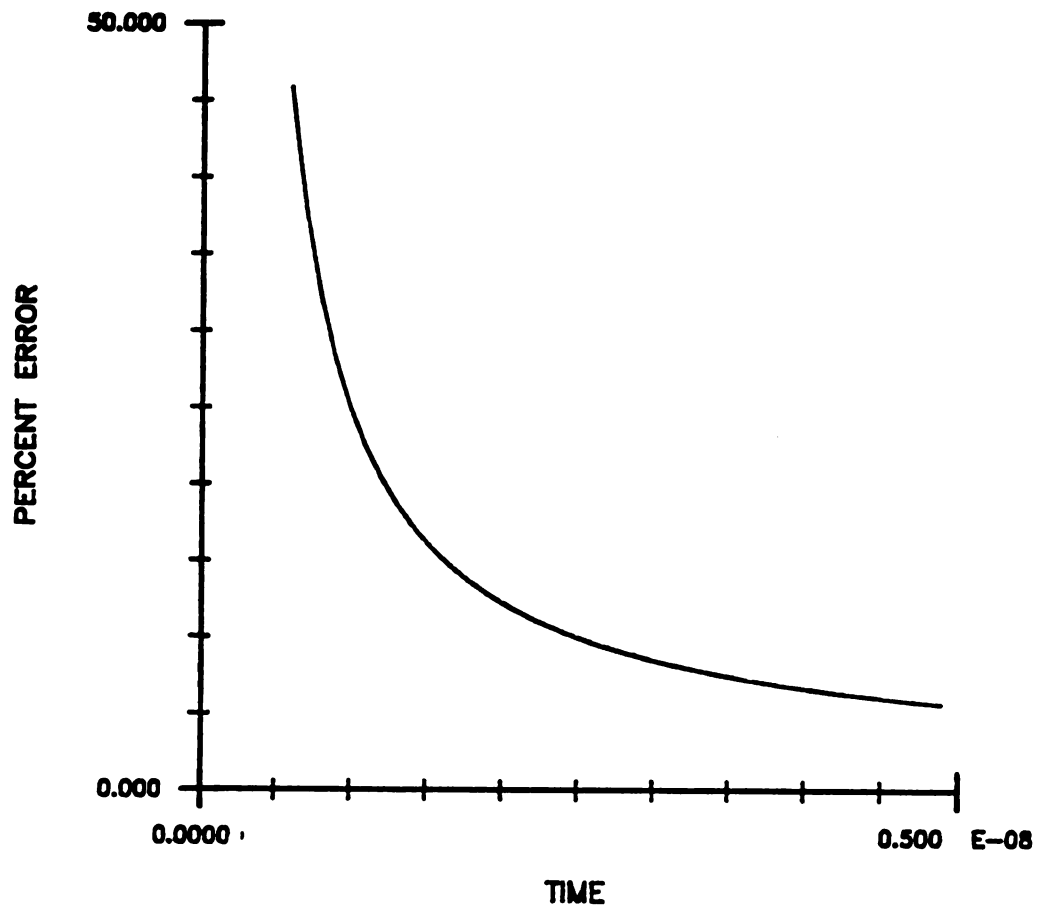


Figure 4 - 6 Error in Rate Model for Multimode Excitation

errors are more serious. The lower limit on the pulse width axis shown in Figure 4-6 is 1 ns. Because of the assumptions made during the derivation of the multimode density matrix equations, their validity for pulse widths less than 1 ns is questionable. For the case of a laser narrowed by an intercavity etalon, having a smaller number of modes, the laser energy is more concentrated, so it saturates the transition more quickly. In this case, as Figure 4-7 shows, the errors for a given pulse width are smaller than for the broader spectrum laser. There are still no pulsations in the excited state population for this case. The errors for the narrowed laser are larger than with the single-mode laser, but much smaller than with the broader laser.

3. Weak Transitions

Frequently, it is not possible to find a transition with a large dipole moment in a convenient section of the optical spectrum. In those cases weaker transitions are used. To test the rate equations model for these transitions the Einstein coefficient, A_{21} , for the modeled transition was decreased by a factor of 100. This serves to model some of the weaker atomic transitions which are useful analytically. None of the other parameters were changed, except those which depend on the value of A_{21} (e.g., B_{12} , μ).

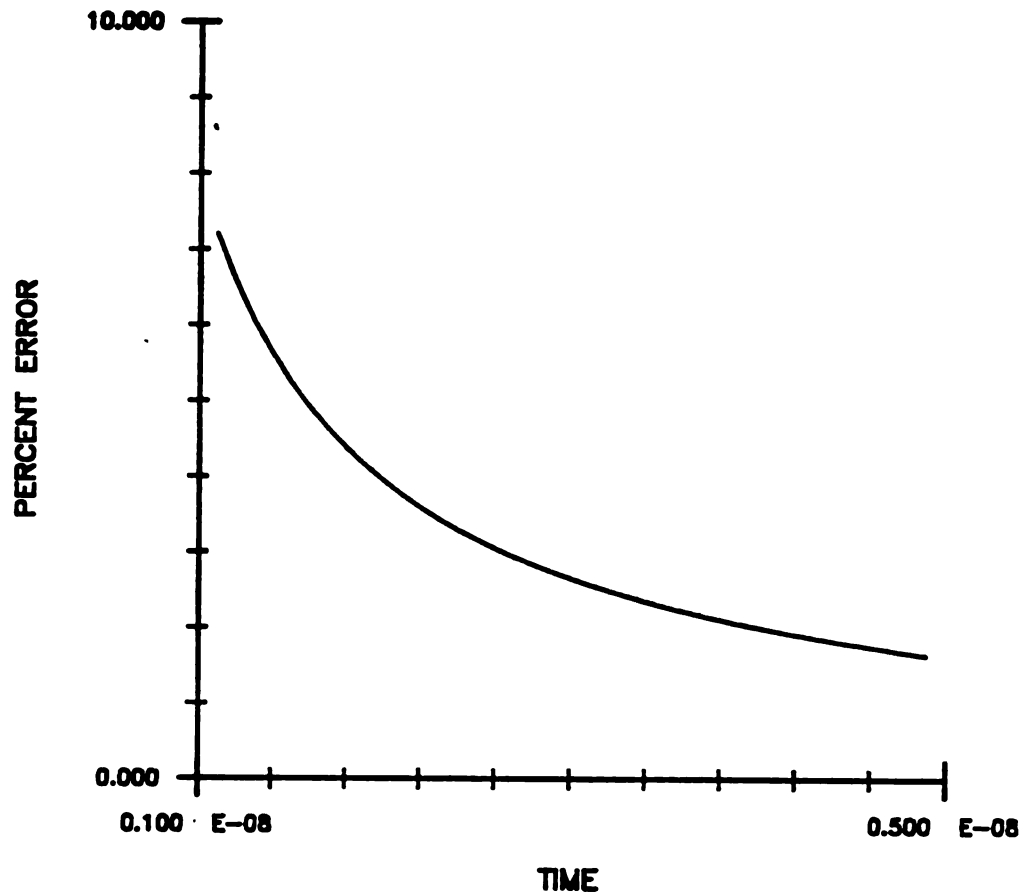


Figure 4 - 7 Error in Rate Model for Spectrally Narrowed Multimode Excitation

a. High laser powers

For the first calculations the laser power modeled was left as 1 MW/cm^2 . Comparison of the results of this section with those of Section D.2. is a comparison of the errors for strong and weak transitions pumped by lasers at high power. Figure 4-8 shows the errors in the rate equation model of the signals for the case of a weak transition pumped by a high powered laser. Because of the high power of the laser, the transition still saturates early in the laser pulse. The errors are within 1% of the errors for the strong transition pumped by the same high power laser. Figure 4-9 shows the same data for the model with an intracavity etalon narrowed laser. Again, because the power is concentrated in a few modes the transition saturates more quickly than when it is pumped with the broader laser. Therefore, the errors are smaller, as they were in the strong transition case. In fact the errors are within 0.3% of those observed with the strong transition model.

b. Low Laser Powers

Chapter III showed that in many cases it is better to use lower laser powers to increase the signal-to-noise ratio in the presence of background ionization. To model the pumping of weak transitions with low power lasers, the laser

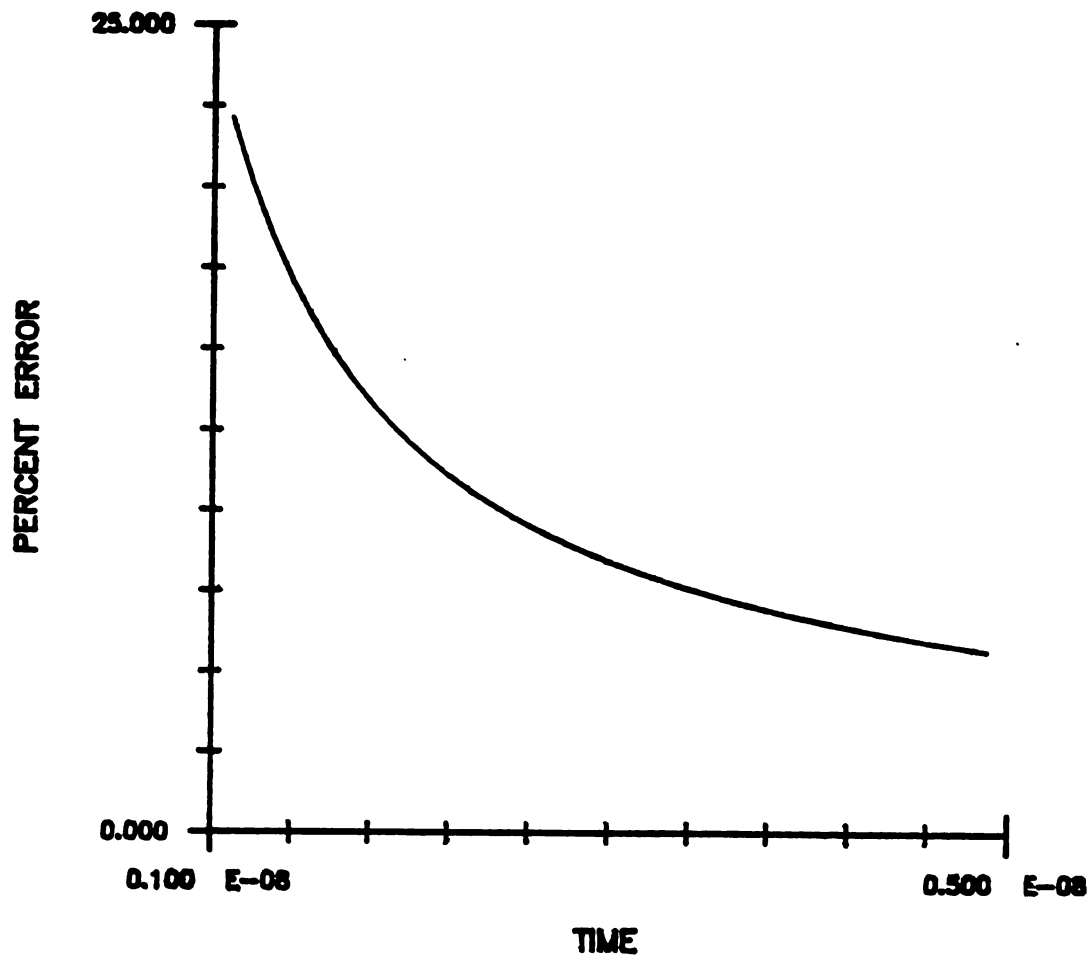


Figure 4 - 8 Error in Rate Model for Weak Transitions
Laser power 1 MW cm⁻².

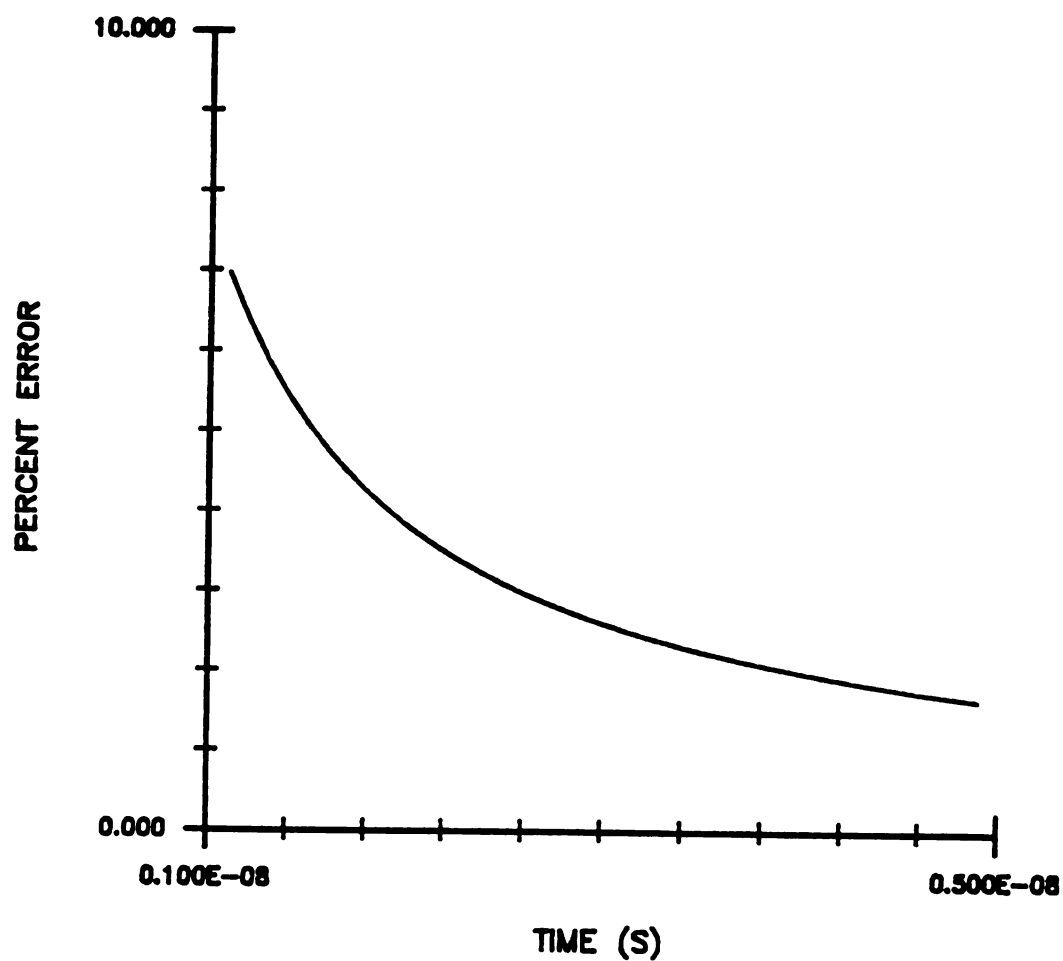


Figure 4 - 9 Error in Rate Model for Weak Transitions, Spectrally Narrowed Excitation. Laser Power 1 MW cm⁻²

irradiance parameter was decreased to 10 kW/cm². In this case the saturation of the ground-to-excited state transition does not occur within the widest laser pulse width being modeled, 5 ns. Saturation in this case would occur with a much longer pulse width. In every case the rate equations predict saturation earlier in time during the laser pulse, if saturation occurs, than predicted by the density matrix model. For these experimental parameters there are large differences between the predictions of the rate equations and the density matrix models. Under these conditions the rate equations predict saturation of the ground-to-excited state transition within about 1 ns, whereas the density matrix does not predict this saturation. The result is the large error shown in Figure 4-10. These results show that it is not accurate to model the pumping of weak transitions of atoms in flames by low-powered, nanosecond-pulsed lasers with rate equations.

4. Effect of Quenching Rates (Flame Type)

The previous sections have all used parameters which describe Ar diluted flames. Many analytical flames use air as the oxidant and therefore are diluted with N₂. Thus, it is useful to examine the effect of changes in the quenching rates on the accuracy of the rate equations model. To model flames diluted with N₂ the collisional quenching rate γ_2 (k_{21}) must be increased significantly. The collisional

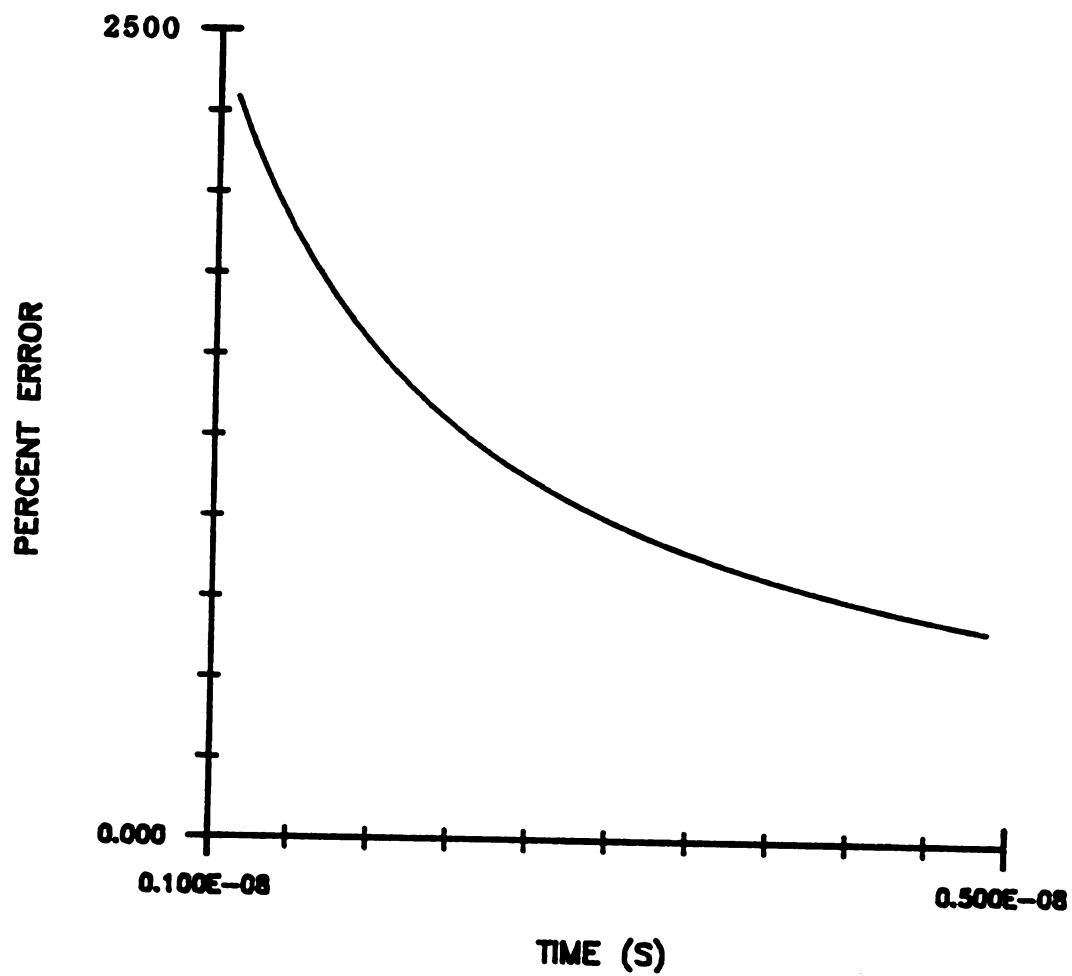


Figure 4 - 10 Error in Rate Model for Weak Transitions
Laser power 10 kW cm⁻².

deexcitation cross section for $\text{Na } ^3\text{P}_{1/2,3/2}$ colliding with N_2 is 10 times larger than its cross section for collisions with Ar. Therefore, for these calculations the deexcitation rate is increased to $1 \times 10^9 \text{ s}^{-1}$. The rest of the parameters used describe a weak transition pumped by a high power laser so that the results of this section may be compared with Section D.3.a. The results are shown in Figure 4-11.

In this case the errors are larger than in the Ar diluted case. This is because the faster deexcitation rate for N_2 diluted flames makes the transition more difficult to saturate; thus, the density matrix requires longer times to achieve steady state. The result is that the errors are larger for a given pulse width, and the errors decay more slowly in time with increasing pulse width than the Ar diluted flame model.

5. Effect of the Dephasing Rate on the Density Matrix Model

In the previous calculations the dephasing rate was held constant at $1 \times 10^{10} \text{ s}^{-1}$. The reason for this can be seen in Table 4-2. The value of γ_{21} does not vary significantly among atmospheric pressure flames. To test the effect that variations in the dephasing rate have on the predictions of the model, its value was varied in the range of 5×10^9 to $2 \times 10^{10} \text{ s}^{-1}$ to cover most transitions in most analytical flames. The other parameters were again the same as Section D.3.a. Increasing γ_{21} to $2 \times 10^{10} \text{ s}^{-1}$ increased

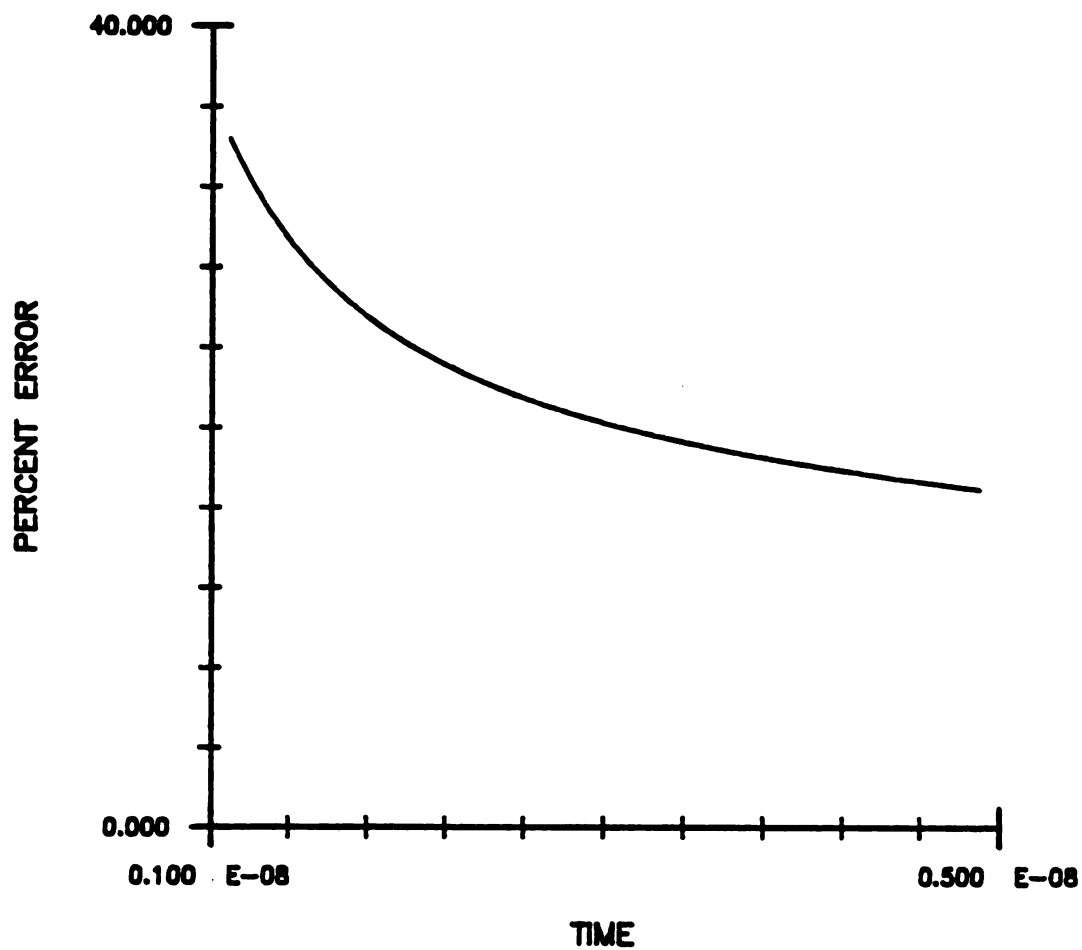


Figure 4 - 11 Error in Rate Model for Highly Quenching Flames. Other parameters as in figure 4-8.

the density matrix predicted ion population by 2.5% after 0.5 ns. The difference was decreasing rapidly with pulse width so that by 1 ns it was negligible. The difference in excited state population predictions was less than 0.5% at 0.5 ns and it was also decreasing rapidly. Decreasing γ_{21} to 5×10^9 caused a greater difference, but the predicted signal only decreased by 6% after 0.5 ns. This difference was also decreasing rapidly with increasing pulse width. For a given pulse width these differences were much smaller than the differences between the density matrix and rate equation models presented in previous sections. Therefore it seems reasonable to use $1 \times 10^{10} \text{ s}^{-1}$ as a mean dephasing rate to model atomic systems in flames.

E. Conclusion

The assumptions inherent in the rate equations model for pulsed laser excitation of bound one-photon transitions require long laser pulse widths to be accurate. The large errors for the case of unsaturated transitions demonstrate this problem. The system needs to achieve a steady state and remain in a steady state long enough to average out the early-in-time errors of the simple rate model's predictions. This time constraint is decreased in the case of saturated transitions. When the laser is powerful enough to saturate the transition early in the laser pulse, the differences in the models' predictions are decreased.

Chapter V

Summary and Future Directions

A. Summary

Two aspects of laser-induced ionization spectroscopy have been examined in the preceding chapters in order to illustrate methods for optimizing the precision of the experiment and to examine theoretical models used to predict ion population motion.

First, methods for maximizing the signal-to-noise ratio for an LII experiment were presented (Chapter III). Models for the signals and noise observed in an LII experiment were derived from rate equations written to describe the ionization process. The noise in LII signals for analyte containing solutions and distilled water were fit with the models in order to find the best-fit values of the model parameters. The models with the best-fit parameters were then used to predict the laser power for maximum signal-to-noise ratio in an LII experiment and to predict the effect of experimental variables on the signal-to-noise ratio and the signal-to-noise ratio versus laser power curve. Two models were developed, one for transitions in the linear or saturated region of the signal versus laser power curve and the other for partially saturated transitions. Background ionization signals and their power dependence and the zero noise were found to be important in determining the laser

power for maximum signal-to-noise ratio. High laser irradiances were found to cause higher background noise levels which decreases the precision of the analyte determination. The next chapter examined the two types of models used to describe the LII experiment on the atomic (or molecular) level, the density matrix formalism and the rate equations. The rate equations are a simplified form of the density matrix derived with the assumption of steady-state density matrix motion. The density matrix models for laser-induced ionization are developed for single mode and multimode laser excitation. The calculated ionization yields for the models were compared to examine the accuracy of the rate equations model for various pulse widths in the range of 1 to 5 ns. The parameters of the models were changed to examine the effect of experimental variables on the accuracy of the rate model. The rate equations were found to give large errors when the transitions being modelled were not strongly saturated. Ion-electron recombination was shown to have little effect on the results of the model calculations.

B. Future Directions

Several studies should help improve the utility and the understanding of LII technique. The noise models developed in Chapter III are useful for determining optimum laser irradiance ranges for single step excitation schemes. The development and testing of models for two-step stepwise LII

schemes, which are commonly used for high ionization potential metals, would aid in the selection of laser powers for these experiments. These models would be more complex and would require noise data for variation of the power of both lasers. The multistep and single step models could then be used to decide between single step excitation schemes, which use high energy ultraviolet photons, and multistep schemes, which use visible radiation. The utility of multiphoton (through virtual states) excitations could also be examined.

The importance of laser r.s.d. in determining the precision of the experiment indicates that the harmonics of the YAG laser [532 nm (2nd harmonic), 355 nm (3rd), and 266 nm (4th)] could be useful as the dominant photoionization laser beam. Because of the lower r.s.d. of these beams powers relative to that of the tunable laser outputs improved signal to noise ratios should be obtained for experiments where these wavelengths could be used to photoionize the excited analyte. It should also be noted that the second harmonic would have the lowest power r.s.d. The power of the ionizing harmonic necessary to insure that photoionization due to its beam dominates that from the exciting laser may, in some cases, be large enough to cause significant background ionization. Experiments need to be performed to examine the trade offs for ionization schemes employing this idea.

Background ionization in all regions of the spectrum of tunable laser radiation should be examined for as many flames as possible. The spectra should also be obtained when solutions of low ionization potential elements, likely to be present as sample matrix constituents, to explore their effect on the background ionization level. Identification of background species would simplify experimental methods for minimizing background ionization. For example, the ionization of NO observed in these studies could be minimized by using a flame which was not diluted with N₂ and which was shielded from ambient air by an Ar sheath flow. Background interferent concentrations could also be mapped out as a function of position in the flame. Because the analyte number density is also a function of position there will be an optimum position which can be located.

The utility of ionization spectroscopy for combustion diagnostics has been demonstrated by the detection of NO, H, and O in flames. The spatial precision with which lasers can be focussed would allow very precise (on the order of 10-100 μ m resolution) mapping of flame species as a function of position. For two wavelength experiments the two beams could be crossed to allow three dimensional mapping of concentration in the flame.

A number of interesting time-resolved experiments could be performed. Measurements of excited state and metastable state lifetimes have been performed in flames by delaying

the ionization laser relative to the exciting laser. Careful choice of the ionization wavelength would allow the study of collisional transfer from the pumped excited state to other excited states with time resolution limited by the laser pulse widths.

REFERENCES

1. P.D. Foote, F.L. Mohler, *Phys. Rev.*, **26**, 195 (1925).
2. F.M. Penning, *Physica*, **8**, 137 (1928).
3. R.B. Green, R.A. Keller, P.L. Schenck, J.C. Travis, G.G. Luther, *J. Am. Chem. Soc.*, **98**, 8517 (1976).
4. R.B. Green, R.A. Keller, G.G. Luther, P.K. Schenck, J.C. Travis, *Appl. Phys. Lett.*, **29**, 727 (1976).
5. C.A. van Dijk, F.M. Curran, K.C. Lin, S.R. Crouch, *Anal. Chem.*, **53**, 1275 (1981).
6. F.M. Curran, K.C. Lin, G.E. Leroy, P.M. Hunt, S.R. Crouch, *Anal. Chem.*, **55**, 2382 (1983).
7. R.A. Keller, R. Engleman Jr., E.F. Zalewski, *J. Opt. Soc. Am.*, **69**, 738 (1979).
8. A. Rosenfield, S. Mory, R. Konig, *Opt. Comm.*, **30**, 394 (1979).
9. F.E. Zalewski, R.A. Keller, R. Engleman Jr., *J. Chem. Phys.* **70**, 1015 (1979).
10. D. Feldman, *Opt. Comm.*, **29**, 67 (1979).
11. C.T. Rettner, C.R. Wevster, R.N. Zare, *J. Phys. Chem.*, **85**, 1105 (1981).
12. S. Wakata, S. Saikan, M. Kimura, *Opt. Comm.*, **38**, 271 (1981).
13. R. Shuker, A. Ben-Amar, G. Ercz, *Opt. Comm.*, **39**, 51 (1981).
14. M.J. Kavaya, R.T. Menzies, U.P. Oppenheimer, *IEEE-J. Quant. Electron.*, **18**, 807 (1982).
15. J. Jirman, W. Durr, *Electron. Lett.* **18**, 69 (1982).
16. S. Yamaguchi, M. Suzuki, *Appl. Phys. Lett.*, **41**, 51 (1982).
17. R.A. Keller, E.F. Zalewski, *Appl. Optics*, **19**, 836 (1980).

18. N.J. Dovichi, D.S. Moore, R.A. Keller, Appl. Optics, 21, 1468 (1982).
19. M.H. Begemann, R.J. Saykally, Opt. Comm., 40, 277 (1982).
20. P. Labastie, J. Phys. B, 15, 2595 (1982).
21. S. Alchalaki, R.S. Stewart, R. Illingwo, I.S. Ruddock, J. Phys. B, 16, 115 (1983).
22. C.R. Webster, R.T. Menzies, J. Chem. Phys., 78, 2121 (1983).
23. C. Dreze, Y. Demers, J.M. Gagne, J. Opt. Soc. Am., 72, 912 (1982).
24. M.J. Kushner, Appl. Optics, 22, 1970 (1983).
25. A.C. Tam, IEEE-Plas. S., 10, 252 (1983).
26. M. Uchitomi, T. Nakajima, S. Mauda, C. Hirose, Opt. Comm., 44, 154 (1983).
27. J.M. Gagne, P. Bouchard, Appl. Optics, 25, 848 (1986).
28. R.C. Carlson, L.A. Cross, T.M. Dunn, Chem. Phys. Lett., 113, 515 (1985).
29. R. Engleman, R.A. Keller, C.M. Miller, J. Opt. Soc. Am. B, 2, 897 (1985).
30. R. Vasudev, R.N. Zare, J. Chem. Phys., 76, 5267 (1982).
31. W.G. Mallard, K.C. Smyth, Combust. Flame, 44, 61 (1982).
32. D.L. Donohue, J.P. Young, Anal. Chem., 55, 378 (1983).
33. L.R. Hess, W.W. Harrison, Anal. Chem., 58, 1702 (1986).
34. R.J. Walker, Anal. Chem., 58, 2923 (1986).
35. U. Kronert, et. al., Appl. Phys. B, 38, 65 (1985).
36. P. Peuser, et. al., Appl. Phys. B, 38, 249 (1985).
37. B.D. Cannon, B.A. Bushaw, T.J. Whitaker, J. Opt. Soc. Am. B, 2, 1438 (1985).
38. F. Kimock, Anal. Chem., 57, 2669 (1985).

39. L.J. Moore, J.C. Travis, J.D. Fasser, T.B. Lucatorto, C.W. Clark, J. Opt. Soc. Am. B, 2, 1561 (1985).
40. C.W. Clark, J.D. Fasset, L.J. Moore, W.W. Smith, T.B. Lucatorto, J. Opt. Soc. Am. B, 2, 891 (1985).
41. B.A. Bushaw, B.D. Cannon, G.K. Gerke, T.J. Whitaker, Opt. Lett., 11, 422 (1986).
42. G.I. Bekov, V.S. Letokhov, V.N. Radaev, J. Opt. Soc. Am. B, 2, 1555 (1985).
43. S.A. Mitchell, P.A. Hackett, J. Phys. Chem., 89, 1509 (1985).
44. A. Sasso, M.J. Schisano, B. Tescione, E. Arimondo, Opt. Comm., 53, 324 (1985).
45. D.H. Praker, **Ultrasensitive Laser Spectroscopy**, D.S. Klinger, ed., Academic Press, New York, NY, 1983.
46. W.G. Tong, R.W. Shaw, Appl. Spec., 40, 494 (1986).
47. T.A. Cool, Appl. Optics, 23, 1559 (1984).
48. D.C. Jacobs, R.N. Zare, J. Chem. Phys., 85, 5457, (1986).
49. D.C. Jacobs, R.J. Madix, R.N. Zare, J. Chem. Phys., 85, 5469 (1986).
50. H. Rottke, H. Zacharias, J. Chem. Phys., 83, 4831, (1985).
51. P.J.H. Tjossem, P.M. Goodwin, T.A. Cool, J Chem Phys., 84, 5334 (1986).
52. J.R. Woodworth, J. Appl. Phys., 57, 1648 (1985).
53. T. Ebata, M. Ito, N. Mikami, J. Chem., Phys., 78, 1132 (1983).
54. K.G. Owens, J.P. Reilly, J. Opt. Soc. Am. B, 2, 1589, (1985).
55. M. Towrie, J.W. Cahill, K.W.D. Ladingham, C. Raine, K.C. Smith, M.H.C. Smyth, D.T. Stewart, C.M. Houston, J. Phys. B, 19, 1989 (1986).
56. D.M. Lubman, R. Tembreull, C.H. Lin, Anal. Chem., 57, 1084 (1985).
57. R. Tembreull, C.H. Sin, P. Li, H.M. Pang, D.M. Lubman, Anal. Chem., 57, 1186 (1985).

58. R. Tembreull, C.H. Sin, H.M. Pang, D.M. Lubman, *Anal. Chem.*, **57**, 2911 (1985).
59. U. Boesl, H.J. Neusser, A.W. Schlag, *J. Chem. Phys.*, **72**, 4327 (1980).
60. D.M. Lubman, M.N. Kronick, *Anal. Chem.*, **54**, 660, (1982).
61. T.G. Dietz, M.A. Duncan, M.G. Liverman, R.E. Smalley, *J. Chem. Phys.*, **73**, 4816 (1980).
62. S. Leutwyler, U. Even, J. Jortner, *J. Chem. Phys.*, **79**, 5769 (1983).
63. R. Tembreull, D.M. Lubman, *Anal. Chem.*, **56**, 1962 (1984).
64. R. Tembreull, D.M. Lubman, *Anal. Chem.*, **58**, 1299 (1986).
65. G.C. Turk, J.C. Travis, J.R. DeVoe, T.C. O'Haver, *Anal. Chem.*, **50**, 817 (1978).
66. J.C. Travis, P.K. Schenck, W.G. Mallard, *Anal. Chem.*, **51**, 1516 (1979).
67. G.C. Turk, J.C. Travis, J.R. DeVoe, T.C. O'Haver, *Anal. Chem.*, **51**, 1890 (1979).
68. R.B. Green, G.J. Harvilla, T.O. Trask, *Appl. Spectrosc.*, **34**, 561 (1980).
69. G.J. Havrilla, R.B. Green, *Anal. Chem.*, **52**, 2376, (1980).
70. G.C. Turk, *Anal. Chem.*, **53**, 1187 (1981).
71. T.O. Trask, R.B. Green, *Anal. Chem.*, **53**, 320 (1981).
72. G.J. Havrilla, S.J. Weeks, J.C. Travis, *Anal. Chem.*, **54**, 2566 (1982).
73. M.A. Nippoldt, R.B. Green, *Anal. Chem.*, **55**, 554 (1983).
74. A.S. Gonchakov, N.B. Zorov, Y.Y. Kyzyakov, O.I. Matveen, *Anal. Lett.*, **12**, 1037 (1979).
75. G.C. Turk, W.G. Mallard, P.K. Schenck, K.C. Smyth, *Anal. Chem.*, **51**, 2408 (1979).
76. C.A. vanDijk, F.M. Curran, K.C. Lin, S.R. Crouch, *Anal. Chem.*, **53**, 1275 (1981).

77. F.M. Curran, C.A. vanDijk, S.R.Crouch, Appl. Spectrosc., 37, 385 (1983).
78. T. Berthoud, J.W. Lipinski, P. Camus, J.L. Stehle, Anal. Chem., 55, 959 (1983).
79. K.C. Lin, P.M. Hunt, S.R. Crouch, Chem. Phys. Lett., 90, 111 (1982).
80. P.K. Schenck, W.G. Mallard, J.C. Travis, K.C. Smyth, J. Chem. Phys., 69, 5147 (1978).
81. W.G. Mallard, J.H. Miller, K.C. Smyth, J. Chem. Phys., 76, 3483 (1982).
82. K.C. Smyth, W.G. Mallard, J. Chem. Phys., 77, 1779 (1982).
83. J.E.M. Goldsmith, J. Chem. Phys., 78, 1610 (1983).
84. J.E.M. Goldsmith, Opt. Lett., 7, 437 (1982).
85. T.W. Hansch, Appl. Opt., 11, 895 (1972).
86. N. Omenetto, P. Cavalli, T. Berthoud, G. Rossi, Appl. Spectrosc., 39, 500 (1985).
87. J.D. Messman, J.D. Parli, N.E. Schmidt, R.B. Green, Appl. Spectrosc., 39, 504 (1985).
88. G.C. Turk, R.L. Watters, Anal. Chem., 57, 1979 (1985).
89. I. Magnusson, O. Axner, I. Lindgren, H. Rubinsztein-Dunlop, Appl. Spectrosc., 40, 968 (1986).
90. O. Axner, T. Berglind, Appl. Spectrosc., 40, 1224 (1986).
91. G.C. Turk, F.C. Ruegg, J.C. Travis, J.R. DeVoe, Appl. Spectrosc., 40, 1146 (1986).
92. B.W. Smith, L.P. Hart, N. Omenetto, Anal. Chem., 58, 2147 (1986).
93. O. Axner, I. Magnusson, Peterson, Sjostrom, Appl. Spectrosc., 41, 19 (1987).
94. G.C. Turk, N. Omenetto, Appl. Spectrosc., 40, 1086 (1986).
95. A. Gaydon, The Spectroscopy of Flames, Chapman and Hall, London, 2nd edition, 1974.
96. G.M. Hieftje, Appl. Spectrosc., 25, 653 (1971).

97. R.J. Krupa, T.F. Culbreth, B.W. Smith, J.D. Winefordner, *Appl. Spectrosc.*, **40**, 729 (1986)
98. **Special Function Analog and Digital Circuits**, National Semiconductor Corp., Santa Clara, CA, 1974.
99. J. Wong, **Application Note 253**, National Semiconductor Corp., Santa Clara, CA, 1980.
100. F.M. Curran, Dissertation, Michigan State University, 1983.
101. E. Voigtman, J.D. Winefordner, *Anal. Instr.*, **15**, 287 (1986).
102. P.D. Wentzell, Dissertation, Michigan State University, 1987.
103. E. Vinter, **Standards in Absorption Spectrometry**, chapter 4, C. Burgess and A. Knowles, eds., Chapman Hall, London, 1981.
104. N. Omenetto, B.W. Smith, L.P. Hart, *Fresenius Z. Anal. Chem.*, **324**, 683 (1986).
105. S.H. Lin, Y. Fujimura, H.J. Neusser, E.W. Shlag, **Multiphoton Spectroscopy of Molecules**, Academic Press, Orlando, FL, 1984.
106. J.W. Daily, *Appl. Optics*, **16**, 2322 (1977).
107. J.W. Daily, *Appl. Optics*, **18**, 361 (1979).
108. K.C. Lin, Dissertation, Ph.D., Michigan State University, East Lansing, MI, 1982.
109. T.J. McIlrath, J.L. Carlsten, *Phys. Rev. A*, **6**, 1091 (1972).
110. C.Th.J. Alkemade, Tj. Hollander, W. Snelleman, P.J.Th. Zeegers, **Metal Vapors in Flames**, Pergamon Press, Oxford, 1982.
111. G.S. Hurst, M.G. Payne, D.S. Kramer, J.P. Young, *Rev. Mod. Phys.*, **51**, 767 (1979).
112. J. Lawton, F. Weinburg, **The Electrical Aspects of Combustion**, Clarendon Press, Oxford, 1969.
113. J.R. Ackerhalt, J.H. Eberly, *Phys. Rev. A*, **14**, 1705 (1976).
114. N.B. Avdonina, M.Ya. Amusia, *J. Phys. B*, **16**, L543 (1983).

115. A.Z. Msezane, J. Phys. B, 16, L489 (1983).
116. M. Aymar, O. Robaux, S. Wane, J. Phys. B, 17, 993 (1984).
117. J. Reader, C.H. Corliss, W.L. Wiese, G.A. Martin, **Wavelengths and Transition Probabilities for Atoms and Atomic Ions**, National Bureau of Standards(U.S.), Washington D.C., 1980.
118. A.N. Hayhurst, T.M. Sugden, Proc. Roy. Soc. Ser. A, 293, 36 (1966).
119. B. Newcombe, C.G. Enke, Rev. Sci. Instrum., 55, 2017 (1984).
120. R. Thiim, unpublished research, Michigan State University, East Lansing, MI, 1985.
121. J.D. Winefordner, W.J. McCarthy, P.A. St. John, J. Chem. Ed., 44, 80 (1967).
122. M.L. Parsons, W.J. McCarthy, J.D. Winefordner, J. Chem. Ed., 44, 214 (1967).
123. C.Th.J. Alkemade, W. Snellman, G.D. Boutilier, B.D. Pollard, J.D. Winefordner, T.L. Chester, N. Omenetto, Spectrochim. Acta, 33B, 383 (1978).
124. G.D. Boutilier, B.D. Pallard, J.D. Winefordner, T.L. Chester, N. Omenetto, Spectrochim. Acta, 33B, 401 (1978).
125. D. Christman, Dissertation, Michigan State University, East Lansing, MI, 1980.

MICHIGAN STATE UNIV. LIBRARIES



31293000567747