# FUNDEMENTAL STUDIES AND APPLICATIONS OF LASER-ASSISTED IONIZATION IN A HYDROGEN - OXYGEN - ARGON FLAME

Ву

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### ABSTRACT

# FUNDEMENTAL STUDIES AND APPLICATIONS OF LASER-ASSISTED IONIZATION IN A HYDROGEN - OXYGEN - ARGON FLAME

By

King-Chuen Lin

Laser-enhanced ionization (LEI) is an application of the optogalvanic effect in flames. A laser is used for resonant excitation of an analyte. Excited atoms subsequently undergo collisional ionization and are detected as ions. This provides considerable enhancement over ground state collisional ionization. Dual laser ionization (DLI) is similar to LEI, but involves two lasers to produce the analyte ions in flames. In our DLI technique, an N2- laser pumped dye laser is used to resonantly excite an alkali analyte to a higher electronic state and then the ultraviolet N<sub>2</sub> laser serves to further promote the excited analyte population into the ionization continuum. Alternatively, collisions in the atmospheric pressure flame may result in ionization of the analyte following the dye laser excitation. The ions produced are collected by a pair of voltage-biased nichrome wires suspended inside the flame, and the signal is

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processed by a boxcar integrator.

This thesis convers two main topics: (1) flame and ion properties probed by DLI, and (2) the relative merits of the DLI and LEI techniques. The first subject includes flame temperature determination by DLI, through the measurement of ion mobility and diffusion coefficients (Chapter V). This is the first time that the optogalvanic effect has been used to measure flame temperature. A current- and voltage-dependent formulation has been derived to characterize the ion production by the laser and to estimate the ion density in the flame (Chapter VI).

On the second subject, two theoretical models based on quantum mechanical methods (Chapter III) and rate equations (Chapter IV) have been studied and compared with the experimental results. Insight is gained with regard to ionization mechanisms, the spectral and temporal profiles of ionization, the relationship of ionization and fluorescence, and the relative enhancement of DLI over LEI. In addition, optimal use of DLI, based on the energy levels of the analyte, has been investigated (Chapter VII). Finally suggestions for the future development of DLI are proposed (Chapter VIII).

# To Dad, to Mom, and to Jueichi

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### CHAPTER I

#### INTRODUCTION

### A. Overview

### A-1 Laser-enhanced Ionization (LEI)

Laser-enhanced ionization (LEI) is a technique to detect analytes in a flame by forming ions with the aid of a laser. Based on the Boltzmann distribution, collisional ion formation in a flame is much less favored from ground state analytes than from excited analytes. Therefore, the laser is employed in the LEI technique to promote an analyte to a higher energy state, so that collisional ionization becomes more efficient. The collisional rate constant is enhanced by decreasing the energy defect between the ionization continuum and the discrete state.

Actually, while investigating the photoionization of alkali elements, Mohler et al., early in 1925, observed Cs ions produced by irradiation of a Cs sample with a wavelength corresponding to the principal series lines of Cs atoms (1). This phenomenon is often called the

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optogalvanic effect. With the advent of powerful lasers, this effect was first applied to analytes in a flame in 1976, and the technique is now more aptly called LEI (2-4). The atmospheric pressure flame used as an atomic reservoir is similar to those used in other analytical atomic spectroscopic techniques. Electrostatic probes have been utilized to detect positive ions and electrons generated in a gas discharge since the 1920's (5). Surprisingly, an instrument consisting of a radiation source (laser), an analyte reservoir (flame), and an ion detector (electrostatic probe), led to a dramatic rediscovery of the optogalvanic effect.

LEI differs from conventional flame spectroscopic methods (such as absorption, emission and fluorescence) and other laser-induced optical methods (such as laser-induced in fluorescence) at least two characteristics. First, LEI involves the continuum states of analytes, whereas other optical methods deal solely with the discrete states; second, an ion detector (electrostatic probe) is employed in LEI, whereas an optical detector (e.g. photomultiplier tube) must be used in the others. Based on these specific characteristics, LEI has been developed as a new, powerful technique in the area of flame spectroscopy. For example, Table 1 compares the detection limits of LEI to those of other optical methods. It can be seen that LEI shows superior sensitivity in trace metal analysis for many elements

A. A. A. A. A. M. H. HERRERARKSTOLENSER
ele- ment	LEI	Faa <sup>a</sup>	FAE <sup>b</sup>	FAF <sup>C</sup>	laser FAFd
Ag	1	1	2	0.1	4
Ba	0.2	20	1		8
Bi	2	50	20000	5	3
Ca	0.1	1	01	20	0.08
Cr	2	2	2	5	1
Cu	100	1	0.1	0.5	1
Fe	2	4	5	8	30
Ga	0.07	50	10	10	0.9
In	0.006	30	0.4	100	0.2
K	1	3	0.05		
Li	0.001	1	0.02		0.5
Mg	0.1	0.1	5	0.1	0.2
Mn	0.3	0.8	1	1	0.4
Na	0.05	0.8	0.1		0.1
Ni	8	5	20	3	2
Pb	0.6	10	100	10	13
Sn	2	20	100	50	
Tl	0.09	20	20	8	4

Table 1. Comparison of Detection Limits (ng/ml)\*

\*Taken from G.C.Turk, J.C. Travis, J.R. DeVoe and T.C. O'Haver, Anal. Chem. <u>51</u>, 1890 (1979).

<sup>a</sup>Flame atomic absorption.

<sup>b</sup>Flame atomic emission.

<sup>C</sup>Flame atomic fluorescence, conventional light sources.

<sup>d</sup>Laser induced flame atomic fluorescence.

(6-8).

# A-2 Current LEI Development

Most LEI research has been carried out by scientists at the National Bureau of Standards (NBS) since 1976; the publications have been recently reviewed (2). Briefly, the mechanism of LEI is as follows: the analyte, nebulized into a flame, is first excited by a dye laser tuned to resonance with a selected excited state; then, the excited atoms are ionized mainly by collisions with in the flame. The collision-dominated foreign gases process is the principal pathway to ionization following resonant excitation of the analyte with a  $\mu$ s pulsed flash lamp-pumped dye laser (4).

LEI, as a new powerful ionization spectroscopy, shows several advantages over other optical methods: (1) LEI is free from certain optical interferences, such as scattering of the laser light, stray light and flame background emission. (2) The efficiency of ion detection can be much higher than that for photon detection; i.e. one ion produced from one atom can in principle be detected by a simple ion probe detector, whereas the quantum efficiency of photomultiplier tube is < 0.50 (3). There are no solid angle restrictions as in fluorescence

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where photons are emitted isotropically. (4) Local dynamics in the flame can be monitored by LEI by positioning the probes and laser beam, but the averaged dynamics are viewed by fluorescence. (5) LEI is free from post-filter effects.

Current developments in LEI can be divided into three main subjects:

(1)Trace metal analysis: this is the major application of LEI. Various approaches have been used to optimize LEI for the detection of trace elements. At present more than 20 species have been measured; detection limits for some elements are as low as 0.001 part per billion (ppb) (e.g. Li) (6-8). The approaches to improving LEI include: (a) use of different types of lasers (CW, pulsed, atomic resonance-line lasers) and dual-dye laser combinations (each dye laser being resonant with a particular atomic transition, and the two lasers sharing a common intermediate state) to upgrade the sensitivity and the selectivity of LEI (6-12). (b) employment of various including single energy schemes photon, two-photon, stepwise and thermally nonresonant processes in efforts to applicability of extend the LEI (6,8,10,12). (c) utilization of various probe configurations and probe shapes in order to increase the ion collection efficiency (4, 13-14).

(2) Electrical interferences in LEI: although the LEI technique is free from many optical interferences, it

is affected to some extent by electrical interferences that originate from thermal ionization of the analyte and matrix species and from combustion reactions in the flame (7,8,11). Flame composition, easily-ionized matrix components, bias voltage applied to the electrodes, probe shapes and laser position with respect to the probes have all been found to affect the LEI signal (7-8, 11, 14-15).

(3) Extension to molecular LEI: investigations in this field have been carried out mainly by another division at NBS. Oxide molecules in a  $C_2H_2/air$  flame can be ionized collisionally or ionized by two photons with resonant irradiation of a dye laser. The ionization the energy defect between process depends on the ionization threshold and the resonantly excited state (16-18). The LEI spectra of oxide molecules were shown to be identical to one photon absorption spectra from the ground state to the resonant intermediate state. Furthermore, the intensity and the resolution (e.g. for the NO molecule) were reported to be better than those from laser-induced fluorescence (16-18). Clearly, LEI can complement conventional optical spectroscopy, not only in trace metal detection, but also in structure elucidation. However, a disadvantage of molecular LEI lies in its restricted applicability; only oxides and a few other molecules (e.g. C<sub>2</sub>, CH) can exist in flames.

There are a few additional papers related to the fundamentals of LEI. Mallard and Smyth obtained ion

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mobilities in  $C_2H_2/air$  and  $CO/O_2$  flames, by measurement of the laser-pulse to the ion-arrival time gap (19). A simple three-level system of LEI has been developed to describe the ion signal production by neglecting relaxation processes from the ions (20). The temporal and spatial behaviors of ions produced by LEI in an  $H_2/air$  flame have been investigated in terms of a unique imaging method (21).

From the above brief review, it is obvious that LEI is not as mature as most optical spectroscopic methods (e.g., fluorescence, emission). The major reason is because of its relatively recent discovery and the small number of groups involved in LEI development at this time; however, it has a very promising future.

# A-3 Dual Laser Ionization (DLI)

Dual laser ionization (DLI) is similar to LEI, but employs two lasers in producing the analyte ions in flames. In our laboratory, the two beams are formed by (a) directing an N<sub>2</sub> laser-pumped dye laser beam and (b) reflecting a portion of the N<sub>2</sub> pumping laser collinearly into the same area of an  $H_2$ -O<sub>2</sub>-Ar flame. The detailed experimental set-up is described in Chapter II.

The idea to use two beams to produce ions in a

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Briefly, in our DLI technique, the dye laser is used to resonantly excite the analyte to a higher energy state. Then the ultraviolet, N<sub>2</sub> laser ( $\lambda$  = 3371 Å) serves as the ionizing beam to further promote a portion of the excited analyte population into the ionization continuum. Alternatively, collisions in the atmospheric pressure flame may result in ionization of the analyte following the dye laser excitation. This is the ionization pathway that occurs in atomic LEI. Because the collisional ionizaiton rate for species present in the excited state is nearly an exponential function of the energy defect between the continuum and the excited state, it can predominate over photoionization if the energy defect is Likewise, photoionization can predominate for small. large energy defects. Thus the energy defect, which depends on the particular excited level, determines which process is dominant. The experimental results and calculated predictions are presented in Chapter VII.

Moreover, the photoionization process in DLI differs from that of the so-called multiphoton ionization spectroscopy (MPI) which is carried out in a low pressure cell. The former requires only on photon from the  $N_2$  laser to achieve ionization; however, MPI involves absorption of N ( $N \ge 2$ ) photons from the laser source, and 'thus requires a more intense laser field to achieve ionization.

#### B. <u>Historical</u>

#### B-1 The Optogalvanic Effect (OGE)

The irradiation of a gas discharge or a flame by light at a wavelength resonant with a transition of the analyte may induce a variation of the impedance which can be detected as a voltage change across the discharge tube or the flame. The rediscovery of this effect with laser irradiation was achieved at NBS in 1976 (3, 24-25). In fact, the OGE was first observed by Mohler et al. and Penning (1, 26-27). Mohler detected Cs ions with a thermionic diode upon irradiation of the Cs with wavelengths corresponding to the principal series lines (1). Penning found the current across the discharge tube changes when radiation from another similar discharge tube was incident (26,27). This was the first observaiton of the OGE in a discharge with a resulting current change in response to the absorption of radiation. Following Penning's observation, several analogous experiments were carried out by various groups (28-32).

Although the OGE was first observed over 50 years ago, the potential of the phenomenon as a detection method was recognized only since its rediscovery by Green et al. (3, 24-25). Green et al. first applied the OGE in hollow cathode tubes to lock a CW dye laser to several characteristic atomic transition frequencies. The voltage change across the discharge tube was used to monitor the wavelength instead of conventional optical detectors (33).

The OGE results make many weak resonance and excited state transitions available for frequency locking (33). King et al. used a similar technique to calibrate the output of a laser and to determine the laser band width (34). Keller et al. calibrated wavelengths emitted by species in a hollow cathode discharge tube through OGE measurements. The correspondence between laser-induced voltage changes and emission intensities permits the establishment of an atlas of emission lines, useful for optogalvanic wavelength calibration (35). Stephens demonstrated that the OGE detector is capable of showing selectivity towards atomic resonance radiation (36). Smyth et al. investigated a possible ionization mechanism for OGE spectroscopy in a neon discharge (37,38). The OGE has

been observed in the discharge of such gas lasers as the He-Ne laser, the xenon laser and the carbon dioxide laser (39-43), and in the subnormal glow discharge of commercial indicator lamps (44).

The OGE spectra of molecules  $(NH_2, NO_2, N_2)$  in a discharge excited with a tunable CW dye laser were first reported by Feldmann (45). His results show that optogalvanic spectroscopy is a simple and sensitive method for the detailed study of the spatial and velocity distribution of plasma atomic and molecular species which cannot be detected by fluorescence spectroscopy without background radiation. Zare and coworkers, reported the OGE in a pure iodine discharge upon irradiation with a CW dye laser (46). The resulting B-X spectrum of  $I_2$  closely resembles the laser-induced fluorescence (LIF) excitation spectrum when the laser beam is off the center line of the discharge axis. In addition, I lines (neutral and ionic) were also found.

High-resolution spectroscopy on single-photon transitions has been performed using Doppler-free intermodulated optogalvanic spectroscopy (47). Doppler-free two photon optogalvanic spectra (TOGS) in a dc discharge tube were reported by Goldsmith et al., who claimed that the method provides a simple and powerful alternative to fluorescence detection of two-photon transition. The result shows TOGS may provide a practical means of observing Doppler-free two photon transitions

from nonmetastable or from metastable states (48).

Ausschnitt et al. reported multiphoton OGE detection of hydrogen and deuterium in a discharge plasma (49). Beenan et al. observed an OGE signal in pulsed hollow cathode discharges (50). The signal in the pulsed mode was increased by factors of 1.7 to 650 over that in a CW mode.

Keller et al. used the laser-induced impedance change in a uranium hollow cathode discharge for standard measurements, for determination spectroscopic of oscillator strengths, for measurement of the electron temperature of the discharge, for isotope ratio analysis and for information about the sputtering process (51). in cesium, argon, neon, Bridges characterized the OGE hyårogen and mercury gas discharge plasmas. The and polarities, magnitude saturation of the induced-voltage changes were determined (52).

Optogalvanic double-resonance spectroscopy was proposed by Vidal as a new method of state-selective spectroscopy applicable to plasma discharges (53). Engleman and Keller irradiated a hollow cathode discharge two lasers with wavelengths corresponding with to different optical transitions in which а common involved (54). intermediate energy level is Their experiments indicated that the induced impedance changes are useful for determining and confirming spectral assignments and for studying energy transfer.

Atomic Rydberg states are usually detected by (1) fluorescence, (2) field ionization, (3) collisional ionization in a space charge limited diode, and (4) The field ionization method, photoionization. in particular, has been used in many experiments involving high-lying states of atomic beams, because the Rydberg states can be easily ionized by a dc electric field, and the ions and the electrons thus produced can be counted almost without loss (55). Bridges first reported a study of the Rydberg states of cesium with the optogalvanic effect and CW laser excitation (52). Camus et al. used the technique to study Rydberg states of barium, with J values ranging from 0 to 5, using a two-step pulsed laser excitation, starting form the  $5d6s^{3}D_{1,2,3}$ , metastable levels populated by the discharge (56). Delsart et al. reported the optogalvanic detection of krypton Rydberg states under two-step pulsed laser excitaiton, starting from either the 2P2, or the 2P3 intermediate level. These states were populated by the first-step N<sub>2</sub> laser-pumped dye laser (57). They have obtained information about the nd  $[3/2]_2$  and nd  $[7/2]_3$  levels, for values of n not accessible to their analogous Kr Rydberg state study with field ionization detection (57,58).

The magnitude of the OGE is dependent on the magnitude of the ionization rates of levels whose populations are perturbed by the laser. Based on this, Lawler developed a linear steady state analytical model of

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the OGE by a rate equation approach applied in a positive column on the 587.6 nm He transition (59).

This review of optogalvanic effect in discharges shows only a few examples of this promising technique. Compared with OGE in discharges, the OGE in flames (LEI) is still in its initial stages of development.

#### B-2 Ionization Spectroscopy with Thermionic Diode Detection

It hard clearly distinguish is to each laser-induced ionizaiton technique. Techniques are typically classified on the basis of the ionization process (collisional or photoionization), the sample type (atom or molecule), the atomization system (discharge, flame, vapor cell, or supersonic nozzle beam) and the detection system (thermionic diode, proportional counter, ionization chamber, electron multiplier or mass spectrometer). These types of ionization spectroscopy are closely related; several of them are discussed in subsections B-2, B-3 and B-4.

Mohler was the first scientist to use a thermionic diode to detect ions. As noted earlier, he monitored the concentration of the cesium ion when the vapor was irradiated with wavelengths of the principal series (1). Because of its high sensitivity, the thermionic diode has

been popularly adapted to measure ion formation (59-61). Typically the thermionic diode contains a plate anode and a dc-heated filament electron source. The amplification factor is in the range of  $10^5$  to  $10^6$ , (comparable to that of photomultiplier tubes); it is ascribed to the trapping of ions within the space charge potential well (62). In a space-charge detector, all the ions created are detected, whereas sample fluorescence emitted isotropically is often detected only over a small solid angle. The current pulse of the thermionic diode are much longer than the excitation laser pulses or the emitted light pulses in a fluorescence experiment. Thus, a fast electronic system is not needed.

Marr and Wherrett employed such a detector with a mercury irradiation of Cs to study the ionization potential of  $Cs_2$ , the ionization processes leading to  $Cs_2^+$  and  $Cs^+$ , and the molecular absorption cross section of  $Cs_2$  (62).

Thermionic diodes have also been employed in the investigation of Rydberg states. Aymar et al. used two-photon absorption spectroscopy with an N<sub>2</sub> laser-pumped dye laser and thermionic diode detection to obtain new data on the even-parity J = 0 and J = 2 levels of neutral barium. The energies of the  $6 \operatorname{sns}^{1} S_{0}$  series ( $16 \leq n \leq 61$ ), the  $6 \operatorname{snd}^{1} D_{2}$  series ( $15 \leq n \leq 81$ ) and the  $6 \operatorname{snd}^{3} D_{2}$  series ( $15 \leq n \leq 81$ ) and the  $6 \operatorname{snd}^{3} D_{2}$  series ( $15 \leq n \leq 30$ ) have been determined (63). Multiphoton ionization of alkali metals with space charge detection

has been investigated by Collins et al. (64).

# B-3 Resonance Ionization Spectroscopy (RIS)

RIS, pioneered by scientists at the Oak Ridge National Laboratory is a photoionization method in which atoms are promoted to an intermediate state with laser(s) radiation and then converted into ion pairs by absorption of photons from precisely tuned laser(s) (22). The electrons produced can be detected either by a pulsed ionization chamber or by a proportional counter. The former is used only as an analog device with a lower limit of sensitivity of approximately 200 electrons; the latter may be used as either a digital or an analog device with a sensitivity of one electron (65,66).

With current laser technology, it is possible to saturate specific transitions and to convert each atom to a positive ion and a free electron. With the aid of a proportional counter the RIS technique was employed to detect a single Cs atom in the presence of  $10^{19}$  Ar atoms and  $10^{18}$  CH<sub>4</sub> molecules (67). Similar experiments were carried out to detect a single xenon atom and a single lithium atom (68,69). Several other applications of RIS, such as photo-dissociation of salts, collisional line broadening measurement, identification of Rydberg states,

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amplification fluctuations in proportional counters, σas and studies of atomic diffusion in the counter have been reported (69-75). P. Lambropoulos has also contributed experimental and theoretical results in the field of atomic multiphoton ionization spectroscopy (76,77). Another branch in this field is being studied in France by Lompre, Mainfray, Manus et al. (experimentalists) and Gontier, Trahin, Crance et al. (theorists) (78-84). In several studies of the multiphoton ionization of atoms, factors such as spatial effects (including the ac stark effect, the enhancement effects, and the effective order nonlinearity) and temporal properties have been of investigated (78-84).

#### B-4 Multiphoton Ionization Spectroscopy (MPI)

In order to avoid confusion with the fields reviewed in subsection B-3, only molecular multiphoton ionization spectroscopy is discussed here. The research groups of Johnson (85,86) and Petty (87) were the first to show that multiphoton ionization spectroscopy (MPI) with a proportional counter or an electron multiplier detection can be a powerful tool to study multiphoton transitions of normal molecules. To date, MPI has been used primarily to discover and identify new electronic states. Examples

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include: iodine, benzene, ammonia, alkanes, amines and where new states can be polyenes predicted --theoretically, but were not previously observable because of the unfavorable selection rules (87-93). In addition, MPI can provide a means of probing excited-state repulsive potentials (94). With MPI, the ionization spectra of the molecules cooled in supersonic nozzle have been a obtained: this greatly simplifies rotational and vibrational structure (95-97). The first studies of multiphoton ionization in effusive molecular beams, with mass analysis to provide identification and relative abundances of the fragmentations, were carried out by Bernstein and coworkers (98,99). From an analysis of the MPI process one can estimate the photon numbers absorbed by the resonant intermediate state (98,99).

# C. Organization of the Dissertation

This thesis contains eight chapters and two appendices. This introductory chapter and the following experimental chapter are general in nature. Theoretical and model treatments, experimental results and applications follow.

Chapter III considers the mechanism of ion production in DLI. The detailed multiphoton ionization

profiles of DLI and LEI with respect to the detuning wavelength are compared with a theoretical model derived from time-dependent perturbation theory. This simplified analysis must be modified somewhat to account for the experimental observations.

DLI and LEI considered are on а more phenomenological basis in Chapter IV through a rate equation approach. The temporal relationship between ionization and fluorescence for the optogalvanic effect in a flame is theoretically described. The predictions have not yet been tested experimentally. In addition, a comparison is made of the enhancement of ionization and fluorescence in DLI to those in LEI, respectively, and of the impact of prolonged irradiation on both DLI and LEI. The rate equation approach can be applied successfully to many aspects of DLI diagnosis.

Chapter V treats the use of DLI to determine flame temperatures. This is the first time that the optogalvanic effect has been applied to measure flame temperatures. Information on ion mobilities and diffusion coefficients in a flame is also provided.

Chapter VI presents further consideration of the behavior of ions in the field of the electrostatic probes. An attempt is made to relate DLI to the probe theories, which have been developed primarily for the diagnosis of gas discharges. A simple model is used to characterize the regions including charged particle sources, sheath and

probe. The behavior of saturated ion current in the field of the probe is described, and ion densities are estimated.

Chapter VII considers the efficacy of the DLI technique. The domination of collisional ionization or photoionization following promotion of the analyte to an excited state can be controlled by selection of the excited state which is in resonance with the tunable dye laser. An examination of which process prevails is made for various selected excited states of sodium and lithium. The results are in agreement with the calculations. Energetic considerations for the optimum application of DLI are discussed.

Suggestions for future development of the DLI technique are presented in Chapter VIII. The DLI-based diagnosis of the temporal and spectral occurrence of excited states is proposed. Also, the possibility of DLI saturation studies and the applicability of DLI in a vapor cell are presented.

Appendix A deals with some basic characteristics of DLI and presents our first experimental results (obtained jointly with C.A. van Dijk and F.M. Curran). Appendix B deals with the calculation of the photoionization cross section of atom based on the quantum defect method. The calculated results by different numerical methods agree with Peach's table of related parameters (100).

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### CHAPTER II

#### EXPERIMENTAL

A. Instrumentation

The basic block diagram of laser-induced а ionization apparatus is depicted in Figure 1. A laser source irradiates the sample and excites the atoms (or molecules); this is followed by absorption of additional photons or by collisions to yield ions. Alternatively, sample ions can be generated by direct multiphoton processes from the ground state. The resulting ions are then collected or counted by an ion detector. Following amplification, the ion signal is recorded by a readout device such as a strip-chart recorder, an oscilloscope or data acquisition system. In computer resonance а ionization spectroscopy (RIS) and the multiphoton ionization (MPI) technique, the sample is introduced in a vapor cell. Typical ion detectors are proportional counters, mass spectrometers, thermionic diodes and electron multipliers (22,62,86,98). By contrast, in laser-enhanced ionization (LEI) the sample is introduced into a flame and biased electrostatic probes are employed



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Figure 1. Schematic laser-assisted ionization apparatus.

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as ion detectors (2-4). Signal processing devices are typically boxcar integrators and lock-in amplifiers for pulsed lasers and CW lasers, respectively.

The dual laser ionization (DLI) apparatus used in this research is analogous to that used in LEI, and is illustrated in Figure 2. The DLI apparatus includes three major components: (1) the light source, composed of a pulsed N<sub>2</sub> laser-pumped tunable dye laser, with the N<sub>2</sub> laser radiation utilized as the second, non-tunable beam; (2) a flame cell as an atom-reservoir, providing a selected concentration of metal atoms; (3) the detection and readout system. The latter includes a pair of biased nichrome wires and a current-to-voltage conversion device for ionization detection, а monochromator (with photomultiplier tube) located at an angle of 90° with respect to the incident light for fuorescence measurement, and a strip-chart recorder and an oscilloscope used as readout devices.

The LEI technique was first developed as a potential trace analysis technique at the Naitonal Bureau of Standards (NBS) (2-3); the NBS workers employed a flashlamp-pumped, s pulsed dye laser or a CW dye laser. The choice of a ns pulsed N<sub>2</sub> laser-pumped dye laser in these experiments was predicated on the following factors:

 The ns pulsed laser source had not been used in previous LEI experiments, and was available in our laboratory.



Figure 2. Block diagram of experimental set-up for DLI.

2. Dual laser ionization may offset the lower ion population induced by a ns pulsed dye laser, as compared to that induced by a  $\mu$ s source. For example, the simple equation  $n \sim k \Delta t$  (n is the ion density, k the ionization rate constant and  $\Delta t$  the laser pulse duration) predicts that the ion population obtained from a 10 ns pulsed laser is less by about two orders of magnitude than that obtained from 1  $\mu$ s pulsed laser, if both lasers have the same power density (W/cm<sup>2</sup>). Thus the N<sub>2</sub> laser-pumped dye laser leads to lower sensitivities in the LEI technique. However, the DLI method may actually show analytical sensitivity superior to that of LEI.

3. Time-resolution of the ion signal can be measured with a ns pulsed laser, and studies of the dynamics of ion behavior are possible.

During the DLI experiment (see Figure 2), the  $N_2$ laser-pumped dye laser was focused in the center of an  $H_2$ -O<sub>2</sub>-Ar flame. A portion of the  $N_2$  laser beam was split off and reflected with a flat mirror into the opposite side of the flame. Both beams are collinearly focused in the same region. The path lengths and lenses were adjusted for maximum temporal and spatial overlap of the two laser pulses at the burner. The ionization signal was detected with a pair of biased,  $\sim 0.9$  mm diameter nichrome wires. These probes were mounted on micrometer-driven transition stages and located in the vicinity of the beam path. The signal from the probes were processed by a boxcar averager

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with gated integrator; data were recorder on an x-t recorder. The fluorescence emitted by the sample was spectrally resolved by a monochromator placed at an angle of  $90^{\circ}$  with respect to the incident laser radiation to minimize the interference of elastically scattered radiation. Following the monochromator, a photomultiplier tube was used to detect the fluorescence. Both the ionization and fluorescence signal could be observed on a storage oscilloscope (Model 564 Tektronix, Inc., Beaverton, OR).

#### A-1 Laser Sources

# (a) <u>N2 Pump Laser</u>

The laser used to pump the tunable dye laser was an  $N_2$  laser with output at 3371 A<sup>O</sup> (Model 0.5 - 150, NRG, Inc., Madison, WI). When the  $N_2$  laser is fired repetitively (10-60 HZ), a train of short pulses (each  $\sim$  5ns FWHM) irradiate a fluorescent dye in the cavity of the tunable dye laser. The general characteristics of the  $N_2$  laser are given in Table 2. During the operation of the  $N_2$  laser, the flow of prepurified grade nitrogen (Airo Inc., Montvale, N.J.) is controlled by a high quality pressure

Table 2. Specifications of Nitrogen Laser

Repetition Rate:	1 - 60 Hz
Peak Power at 60 Hz:	0.5 MW
Pulse Dration:	5 nsec FWHM
Average Power at 60 Hz:	150 mW
Power Requirement at 120 volts, 60 Hz:	10 amp
Beam Divergence:	3.8 mrad x 10.7 mrad

regulator (also Airco) having both high and low pressure gauges; the low pressure gauge is used to set the pressure in the spark gap, which normally operates in the pressure range of 20 to 28 psi. The following  $N_2$  passes through the spark gap, then through the laser tube where the pressure is adjusted to be about 70 Torr by a needle valve. A filter dryer is located between the spark gap and the laser tube in order to remove any carbon that may be released in the spark gap. A diagram of the flowing nitrogen system is shown in Figure 3. A water on-off valve is located on the input side of the power supply. This interlock protects against operation of the laser without water cooling.

The conditions used in the experiment maintain the laser tube pressure at 70 Torr, the pressure in the spark gap at 25 psi, and the repetition rate of the laser at 20 Hz. These conditions provide satisfactory output power and stable peak-to-peak ratio. The pressure in the N<sub>2</sub> laser tube affects the output power of the N<sub>2</sub> laser, and thus that of the dye laser; subsequently, it also affects the sensitivity of ionization induced by the N<sub>2</sub> laser-pumped dye laser. The ionization signal, and the power output of dye laser versus N<sub>2</sub> pressure in the laser tube are shown in Figure 4.


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Diagram of flowing nitrogen system for N<sub>2</sub> laser. A, N<sub>2</sub> bottle; B, regulator; C, spark gap; D, filter dryer; E, needle valve; F, vacuum gauge; G, laser; H, vacuum pump. Figure 3.



Figure 4. Dependence of dye laser power ( $\circ$ ) and sodium ionization ( $\Delta$ ) on N<sub>2</sub> pressure in N<sub>2</sub> laser tube. The ionization signal of sodium is related to the dye laser power. Sodium ions are produced by dual laser ionization (DLI) with the dye laser tuned to a transition of the 3S<sub>2</sub> + 3P<sub>3/2</sub> level of sodium. The concentration of sodium is 10 ppm (µg/ml).

Ъ. : : 111 ...... :.... 2; ¥.: ..... : 3 1 . 943  (b) <u>N2</u> Laser-Pumped Dye Laser

The dye laser was first discovered by Sorokin and Lankard in 1966 in describing the stimulated emission from a fluorescent organic dye in liquid solution and by Schäfer et al. in realizing the tunability of such a source (101,102). Since then, the dye laser has been highly developed. It offers a simple and versatile method for generating tunable, coherent radiation over a broad range from the ultraviolet to the infrared. Several properties of optically pumped dye lasers are described below:

(1) frequency range: The output tuning range of a dye laser, usually pumped by a fixed wavelength laser, depends mainly on the particular dye or dye mixture used in the laser. This range may vary from several nanometers to over a hundred nanometers. Figure 5 depicts the wavelength ranges for various dyes when pumped by an  $N_2$  laser.

spectral width: The linewidth (FWHM) (2) of the simplest dye laser configuration is on the order of 5 nm. This width can be reduced dramatically by adding a spectral resolution element, such a prism, as a interference filter or diffraction grating, an а Fabry-Perot etalon. For example, a linewidth of 0.01 Å for an N2 laser-pumped dye laser was obtained by using a



(From the catalog of the exciton Corp., Dayton, The wavelength range of various organic dyes pumped by a 337.1 nm, N<sub>2</sub> laser (Molectron) . (но Figure 5.

telescope in the optical cavity, together with a grating and an etalon (103); the typical value is on the order of 1 to 10  $\mathring{A}$  when a single diffraction grating is employed for tuning (104).

(3) pulse duration: Typically, the pulse duraiton of flashlamp-pumped dye lasers is on the order of  $\mu$ s, and that of N<sub>2</sub> laser-pumped dye lasers is on the order of ns. Through mode-locking techniques, the pulsed or CW dye laser can be broken up into a train of very short pulses, on the order of ps (105,106).

(4) power and energy: A typical specification of a flashlamp-pumped dye laser is a 10-100 mJ energy output in a 0.3 to 1  $\mu$ s pulse with a repetition rate of 10-100 HZ. Thus the average output power is on the order of 1 W, and the peak output power is on the order of 100 KW (107). In contrast, the N<sub>2</sub> laser-pumped dye laser has a typical output energy of 10  $\mu$ J - 1 mJ and a pulse duration of 2-8 ns (103). The peak output power of dye lasers pumped by an N<sub>2</sub> laser is also on the order of 100 KW, although the pulse energy is less than that of flashlamp-pumped dye lasers.

The block diagram of the  $N_2$  laser-pumped dye laser employed in these experiments is illustrated in Figrue 6. For such Hänsch-type dye lasers, the cavity is constructed by a front mirror and a diffraction grating, which is used as the wavelength tuning element. A cylindrical quartz lens focuses the  $N_2$  laser beam to a narrow line inside the



dye cell. The subsequent fluorescent radiation is collected by an achromatic telescope which also expands the beam before it reaches the grating, thereby causing a larger fraction of the grating surface to be illuminated providing a consequent reduction of the output and radiation bandwidth. Similarly, the second order of the plane diffraction grating (lines/mm = 1180, blaze  $\lambda = 2500$ A) is used to reduce the output pulse bandwidth. The output power can be measured by a joulemeter (Model J3 -05, Molectron Corp., Sunnyvale, CA) connected to an oscilloscope; the temporal dependence of the pulse can be observed on the oscilloscope by using a photodiode to convert the radiation into an electric signal.

The properties of the dye laser with Rhodamine 6G, one of the laser dyes used in these experiments, are characterized by the following:

(1) frequency range: The Rhodamine 6G dye laser covers a range of  $20 \sim nm$  ( $\sim 10$  nm FWHM). The laser output power as function of wavelength is plotted in Figure 7.

(2) spectral width: The bandwidth of the dye laser, with Rhodamine 6G, is about  $0.7 \pm 0.1$  Å. This value was obtained by two different methods: laser-induced atomic fluorescence and dual laser ionization. These methods are described in detail in Chapter III.

(3) pulse duration: A pulse length of 3-4 ns (FWHM) is obtained.

(4) peak power: Peak output powers of  $\sim 45$  KW (or



The output power distribution of dye laser (Rhodamine 6G) with respect to wavelength. A strip chart recorder is employed as the readout device. The dashed line (---)
indicates the residual power caused by broad band
lasing of the organic dye. peak energy  $\sim 160 \mu J$ ) at 5890 Å and  $\sim 85 KW$  (or peak energy  $\sim$  300  $\mu J$ ) at 5787 Å can be achieved.

In order to increase the power density of the laser, a lens with 15 cm focal length was set at an appropriate position between the front mirror and the flame. The cross section of the beam waist focused by the lens was measured with a 50  $\mu$  m pinhole moved in three dimensions by a micrometer-driven translation stage. At first the pinhole was moved along the Z axis, the direction of the laser beam, and fixed at the position with the maximum output power as measured by the joulemeter; then the pinhole was moved in the X and Y directions, respectively. A spatial profile of output power against the X (or Y) axis was obtained, as shown in Figure 8. By multiplying the full width at half maximum (FWHM) of the Gaussian profiles obtained in the X and Y axes, respectively, an effective cross section of the beam waist  $(cm^2)$  was estimated. The focal area of the dye laser through the lens was determined to be (1.0  $\pm$  0.3) x 10<sup>-3</sup>  $cm^2$ ; similarly, the focal area of the N<sub>2</sub> laser through a quartz lens was determined to be  $(2.0 \pm 0.4) \times 10^{-4} \text{ cm}^2$ .

Although we may take full advantage of the high output power, the short pulse duration and the small spectral linewidth of the  $N_2$  laser-pumped dye laser in these experiments, several disadvantages exist:

(1) The tunable frequency range of each dye is small. In order to excite different elements, many

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Figure 8. Measurement of the effective cross section of beam waist of  $N_2$  laser along the X axis (the direction parallel to the optical table, but perpendicular to the laser beam). A joulemeter is used to monitor the power output of  $N_2$  laser by irradiation through a 50 µm pinhole moving along the X axis. The pinhole is positioned by a micrometer-driven translation stage. Full width at half maximum (FWHM) of the laser beam is estimated to be 220 µm. different dyes must be used and an appropriate optical alignment is required to maintain a maximum output power for each dye.

(2) Each dye solution has a finite lifetime. Degradation of the dye solution and a consequent reduction in output power were noted during long-term experiments. The ouput power of the dye laser also depends on temperature. Peters et al. pointed out that at temperatures higher than  $\sim 20$  °C, the peak power of Exciton C460 drops to  $\sqrt{70}$  of the original power and the divergence angle of the laser beam increases by  $\sim 13$ % (108). Fortunately, this effect is small for the dye solutions selected in our experiments.

(3) High intensity radio frequency interference (RFI) is generated, which introduces noise into other electronic devices operated in the vicinity. For this reason, two rf chokes, consisting of several wire turns around a ferrite core, were soldered into the high-voltage power line of the  $N_2$  laser. Both the laser and the chokes were placed inside a grounded Faraday cage, consisting of 0.5 mm copper plating. These measures substantially decreased the RFI from the  $N_2$  laser discharge.

(4) Large pulse-to-pulse variations of about 10% in the laser output.

(5) A significant background of broad band lasing from each dye solution is generated (see Figure 7). Such lasing may interfere with the ionization signals,

especially those induced by the DLI process; fortunately, the wavelength range of broad band lasing is invariant and several hundred  $\stackrel{\circ}{A}$  away from the selected wavelength. By selecting carefully the baseline, we may avoid its interference with the DLI signal. This is discussed in detail in Chapter VII.

## A-2 Flame Cell

The laminar flow, premixed, H<sub>2</sub>-O<sub>2</sub>-Ar flame utilized in the experiments is illustrated in Figure 9. Prepurified grade gases:  $0_{2}$ ,  $H_{2}$  and Ar, are controlled by dual pressure regulators, having high and low pressure stages. After passing through the pressure gauge, each gas is divided into two branches which form the inner and mantle flames, respectively. By adjusting a control valve to provide a predetermined setting on each calibrated flowmeter, a selected flow rate (1/min) for each gas can be obtained. For each branch of the flame, 02 and Ar are premixed first in a mixing chamber fitted with a safety spring; the subsequent gas mixture then mixes with  $H_2$  in another chamber prior to reaching the burner head. In this way, spontaneous combustion of  $H_2$  and  $O_2$  inside the mixing chamber can be safely avoided. The atomic analyte is introduced into the inner flame by carrying its salt



Figure 9. Elock diagram of gas flow system in an H<sub>2</sub>-O<sub>2</sub>-Ar flame. CYL, high pressure cylinder; HPR, high pressure regulator; CV, capiliary valve; FM, flow meter; Spr, sprayer; MC, mixing chamber; WB, washing bottle; B, burner house.

solution out of a pneumatic nebulizer with Ar gas (see in Figure 10) before mixing with other gases. The mantle flame has the same composition as the inner flame, but contains no metal salt.

The laminar premixed  $H_2-O_2-Ar$  flame is one of the most important premixed flames (109,110). Two important properties of the flame are:

(1) Low flame background emission, and low temperature resulting in less ionization interference.

(2) A high quantum yield for fluorescence, because the quenching cross section of Ar is very small (< 2  $\dot{A}^2$ ) (111). Essentially, laminar premixed flames are less turbulent, less audibly noisy and have less flame flicker each flame gas is than turbulent flames, in which introduced separately and mixed above the burner head (112). Accordingly, the  $H_2-O_2$ -Ar flame results in less electrical interference from ionized combustion products in ionization experiments, and provides an intense signal signal-to-noise ratio fluorescence with high for measurements.

The burner of the flame is of the Méker type; the gases reach the burner head through 631 circular holes of 0.5 mm diameter and 5 mm length, arranged in concentric circles with a 2 mm interval between successive rings. The diameter of the inner flame is 15 mm, and the height of the primary combustion cones is approximately 2 mm. The burner head is cooled by a water jacket (113).

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In comparison to the ultrasonic nebulizer or the Hieftje-Malmstadt type nebulizer (114), the homemade pneumatic nebulizer used in this work produces larger droplets and less spatial resolution, which may result in optical scattering or imcomplete vaporization of solvent or solute. Nevertheless, DLI and LEI suffer no optical interference from flame background or stray light. Thus the disadvantage of the nebulizer is negligible in ionization experiments.

The mantle flame prevents entrainment of air and smooths the radial temperature distribution of the inner flame. The effect of the mantle flame on the ionization signal is insignificant. However, if the mantle flame is higher temperature than the inner flame, energy of transfer to the inner flame can occur, which results in a disturbance of local thermodynamic equilibrium. Thus the mantle flame should be as identical in temperature to the inner flame as possible. Strictly speaking, in a flame or other high temperature plasma, it is impossible to reach true thermodynamic equilibrium because the flame radiates heat to the environment, undergoes secondary combustion at the flame boundaries and undergoes convection; these processes lead to a net transfer of heat, mass and radiation within the flame. However, even though these transfers occur within the flame gases, it is still possible to maintain a "local" thermodynamic equilibrium as long as the transfer rates are small compared with the

rates of equipartitioning of energy over the different energy forms. In a laminar premixed flame the region of a local thermodynamic equilibrium can be extended over a considerable portion of the flame gases; in contrast, the local equilibrium region is very small in the turbulent flame (115,116).

When the inner and mantle flame have the same flow rate of  $H_2$ ,  $0_2$  and Ar (equal to 1.0 l/m, 0.5 l/m and 3.2 l/m, respectively), the temperature was determined by the DLI method to be about 2100 K, which satisfactorily agrees with that obtained by line reversal methods in similar flames. Flame temperature measurement by the DLI technique is described in detail in Chapter V.

In all atomic flame spectrometric methods, a sample solution is aspirated into the flame to produce an atomic vapor. There are five basic steps occuring throughout the process:

(1) solution transport: In the initial step, the solution is carried from a container into the nebulizer.

(2) droplet formation: The salt solution is broken into droplets after reaching the nebulizer; the size of the droplets formed decreases as the solution uptake rate increases.

(3) solvent evaporation: The solvent evaporates from the droplet to leave a salt particle (This step may be completed with a chamber type nebulizer, such as pneumatic and ultrasonic nebulizers, before the analyte

reaches the flame.). The rate of solvent evaporation depends on several factors: the size of the droplet, the characteristics of the solvent, the number of solvent droplets per cubic centimeter and the flame characteristics.

(4) solute evaporation: The remaining salt mist evaporates at a rate dependent on the size of the salt particles, the number of salt particles, the characteristics of the salt particles and the flame characteristics.

(5) atomization: The final step is the production of atomic vapor after the solution is introduced into a flame. The free atom fraction is the ratio of the concentration of analyte species in the form of atoms to the combination of analyte in all forms such as ion, oxide and hydroxide.

A general expression relating atomic concentration N in the flame gases to the analyte concentration  $C_0$  in the solution sprayed into the flame is (112,127):

$$N = (6 \times 10^{23}) \frac{F \varepsilon \beta C_0 g}{Q_t e_f Z_T}$$
(1)

Here F indicates the solution transport rate  $(cm^3/sec)$ ;  $\varepsilon$ is related to the sprayer efficiency  $\varepsilon_{spray}$  and the degree of solute vaporation  $\varepsilon_{sols}$ ;  $\beta$  is the free atom fraction; g is the statistical weight of the ground state;  $Q_t$  is the flow rate of unburnt gases into the flame;  $e_f$  is the

expansion factor for the flame gases;  $Z_T$  is the normalized electronic partition function. The atomic concentration N is a linear function of the analyte concentration over a wide concentration range. This is demonstrated in Figure 10 for thermal emission vs. sodium concentration in sodium chloride solutions; the deviation from linearity around 200 ppm is mainly due to the decrease in sprayer efficiency ( $\varepsilon_{spray}$ ), as the analyte concentration increases, or to self-absorption.

## A-3 Optical Detection

The optical detection system used in these experiments consists of a filter/grating double monochromator (Model EU 700-56, GCA, Mcpherson), coupled to a photomultiplier tube (Model EU 701-30, GCA, Mcpherson), located at an angle of 90° with respect to the incident laser beams. The analyte fluorescence from the flame is lens onto the entrance slit of the focused by a The resolution element is monochromator. a plane diffraction grating. (48 mm x 48 mm ruled area; lines/mm = 1180, blaze  $\lambda = 2500 \text{ \AA}$  ). The monochromator has an assembly of eight filters with controlled spectral transmittance characteristics, which provide a preliminary stage of wavelength discrimination. This feature serves to reduce



- Figure 10. The concentration dependence of thermal emission of sodium atom in an  $H_2-O_2$ -Ar flame. An RCA IP 28 photomultiplier tube (no filters) is used as detector. The applied voltage is 700 V. The thermal emission signal tends to deviate from the linearity when the sodium concentration becomes > 100 µg/ml due to self-absorption and nebulizer inefficiency.

higher order diffracted radiation and stray light, resulting in higher purity of the measured fluorescence signal. The spectral band pass of the monochromator is 2 Å when a 100  $\mu$ m slit width and 1 mm slit height are employed. It is possible to reach 0.3 A spectral resolution with a 5  $\mu$ m slit width and 1 m slit height (118).

A photomultiplier tube (RCA, IP 28A) was set right behind the exist slit to detect the incident radiation alreadv spectrally resolved by monochromator. The photomultiplier tube (PMT) typically has a wide linear dynamic range of about 10<sup>6</sup> or more (112,119); nonlinear response ensues as the photomultiplier approaches saturation, which is caused by space charge limitations at the last few dynodes, and by finite photocathode resistivity effects (120). The nonlinear behavior can be easily checked by inserting a set of neutral density filters in front of the entrance slit of monochromator. The bias voltage between the anode and photocathode was set to -800 volts. The output current of the PMT was converted to a voltage and processed by a boxcar integrator. The output of the boxcar was read out on a strip chart recorder.

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## A-4 Ionization Detection

The alkali metal ions produced in the flame by the DLI or the LEI technique are collected by a pair of voltage biased nichrome wires suspended inside the flame, about 10 mm above the burner head in order to avoid the combustion zone close to the burner head. The probe current passes through an electronic circuit formed by a preamplifier and a high-pass filter. The resulting voltage output is the input to the boxcar integrator for signal processing. The nichrome probes ( $\sim 0.9$  mm in diameter) are inexpensive and resist satisfactorily the high temperature environment of the flame. The probes last several hundred hours. The disadvantage of using nichrome probes results from analyte contamination, which grows gradually on the probe surface upon continued use. Leaching from the probe may lead to significant electrical interference upon the ionization signal when different analytes are introduced into the flame. Therefore, probes are changed often to avoid this interference.

The nichrome wires were positioned parallel to one another in a plane perpendicular to the burner head. The probes were typically 4-10 mm apart. The bottom probe was placed about 10 mm above the burner head, and was mounted on a micrometer-driven translation stage with a positional accuracy of  $\pm 0.01$  mm; the top probe was also mounted on an

e. ••• i 70 •1 :: ÷ ..... -0 2 . • 1 3 <u>}-</u> 10 57¢ ÷. :: e electrode holder and was movable in three dimensions by tuning an adjustment knob. The ionization sensitivity was found to have an unsymmetrical response to the probe voltage polarity. Superior sensitivity was achieved when the bottom probe was biased negative with respect to the top probe and located closer to the irradiated area. A detailed discussion of the ion behavior in the field of the probes is given in Chapter VI.

The advantage of using metal wires to collect the ions is one of convenience and economy. Such electrodes are suitable for high temperature flames, although different ionic species cannot be distinguished. However, by using a high resolution laser source, the DLI technique can compensate for this disadvantage.

## A-5 Signal Processing

The output signal from the ion detector or the photomultiplier tube is the input to a dual channel boxcar averager (Model 162-164, Princeton Applied Research Corp., Princeton, N.J.) for signal processing. A boxcar averager can increase the signal-to-noise ratio by repetitive sampling of the signal-plus-noise with a gate at the appropriate time after a trigger pulse. It is advantageous to employ a boxcar averager to manipulate a signal induced

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The boxcar averager was triggered synchronously by radio frequency noise produced when the N<sub>2</sub> pumping laser is fired. There is a delay of  $\sim$ 75 ns before the boxcar aperture opens to manipulate the signal. The lifetime of ions produced by the laser pulse is on the order of μs. Hence it is not necessary to employ a delay line to prevent the signal from appearing prior to the gate. However, the lifetime of atomic fluorescence is on the order of ns; in this case, a delay line is useful. Since no impedance transformer device is employed at the output of photomultiplier tube to maintain the "true" signal throughout the delay line, the fluorescence profile will be distorted to some extent (121). Since the fluorescence profile is not a major emphasis of this work, this distortion was neglected.

The dual channel boxcar averager main frame (model 162) is equipped with one model 164 gated integrator and one model 163 sampled integrator which incorporates a Tektronix S-2 sampling head. The gate width of the model 164 provides a continuously variable sampling gate from 5 ns to 5 ms width. In contrast, the model 163 utilizes a selection of plug-in sampling units to obtain nonadjustable sampling gate widths ranging from 75 ps to 1

ns (122). Consequently, the model 163 is preferably employed to sample a fast signal such as ns fluorescence decays. However, for time-integrated signals or for longer decay times, the model 164 is preferred because its variable gate width can be adjusted to obtain a maximum signal-to-noise ratio. Accordingly, the model 164 gated integrator was employed to manipulate all the ionizaiton decays, on the order of  $\mu$ s, and the time-integrated ion signal and fluorescence signal in these experiments. Although a baseline sampling gate, associated only with the model 163, would be useful to eliminate the distortion caused by baseline drift on time-scanned signals, such distortion seemed negligible in these experiments.

The sampling gate of both the model 163 and the model 164 can be positioned anywhere along the signal waveform, or it can be time-scanned across all or a portion of the signal by adjusting the initial dial. For averaging at a fixed point in time, hereafter called single-point analysis, the gate was located so as to encompass the peak maximum.

There are two modes, exponential averaging and sum averaging, incorporated in the model 164. When operating in the sum averaging mode, the result of each integration is added linearly to the previous values until output overload occurs. The output in this mode is simply the average of N repetitions; for white noise the signal-to-noise ratio should improve with  $\sqrt{N}$ . The mode is

only employed in single-point analysis. The summing mode is analogous to linear integration with an analog integrator. When the exponential averaging mode is chosen, the output signal asymptotically approaches G times the input signal, where G is a gain factor. When the output level reaches G times the input level, there is no further output signal, no matter change in the how many repetitions of the input signal occur. Accordingly, it is considered to be the average of 2TC/AD repetitions of the input signal, where TC is the selected model 164 time constant and AD is the selected aperture duration. The signal-to-noise ratio achieved by this mode is  $(2TC/AD)^{1/2}$ The exponential mode is analogous to low-pass filtering with an RC filter.

The exponential mode can be used in both singlepoint analysis and time-scanned analysis. For the latter with the model 164, the minimum scan time (MST) is determined by

$$MST = 5 \left[ (SPTC)^2 + (OTC)^2 \right]^{\frac{1}{2}} \times \frac{ADR}{AD} , \qquad (2)$$

where the signal processing time constant (SPTC) is selected by the main frame time constant switch, the observed time constant (OTC) is computed by dividing the selected model 164 time constant by the product of the aperture duration times the repetition rate; ADR is the aperture delay range and the value of AD is the aperture

duration. For example, for one of the experimental conditions used here, the repetition rate was 20 HZ, the ADR was 50  $\mu$ s, the AD was 0.5  $\mu$ s, the SPTC was 100  $\mu$ s and the time constant of the model 164 was 10  $\mu$ s. The minimum scan time was thus estimated as 500 sec.

The spectral profile of ionization is obtainable with single-point analysis by averaging the portion of signal within the gate, then varying the laser wavelength across the signal profile. The temporal profile of ionization can be obtained by time scanning the boxcar gate across a portion or all of the ionization decay. Single-point analysis and time-scanned analysis are related to each other; that is, the spectral profile of ionization can be obtained by time-scanned analysis and the temporal profile can be obtained by single-point analysis. For each point (or wavelength) on the spectral profile of ionization, there is a corresponding temporal decay obtainable by scanning the gate width across the pulse formed at each different wavelength. The time can be integrated on a strip chart recorder at each wavelength; a gain G is related to the resulting area and timeintegrated value obtained from single-point analysis. The area integration can be computed by applying cubic spline interpolation to several selected known points to derive a decav function associated with the temporal profile obtained experimentally. A computer program DCADRE (from the IMSL routine library) was utilized to integrate the

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function. Figure 11 shows a comparison of the area integrated spectral profile to the time-integrated profile for the ionization of sodium induced by DLI with  $3S_{1/2}$  - $3P_{1/2}$  absorption. The methods are in satisfactory agreement. A significant error encountered with cubic spline interpolation is caused by the difficulty in selecting data around the maximum; however, manipulation of several sets of data may compensate for this drawback.

On the other hand, the sampling gate can be positioned along the inization signal waveform by adjusting the initial dial, as mentioned earlier. For example, if the aperture delay range (ADR) is 50  $\mu$ s, and the intial dial is set at 10%, then the aperture delay is 5  $\mu$ s; that is, the aperture opens after 5  $\mu$ s delay within ADR. Consequently, it is possible to obtain a temporal profile of the ionization signal by serially positioning the aperature at points on the input waveform, then averaging the intensity at each point. By varying the value of the initial dial, the relative position of each average value carried by single-point analysis along the waveform of the pulse can be counted. A comparison of the temporal profile of ionization estimated by such a method with that obtained by time-scanned analysis is also given in Figure 12. The lifetimes of the ionization signal obtained by single point analysis are 3.2  $\pm$  0.2  $\mu$ s and 3.6  $\pm$ 0.2  $\mu$ s under the conditions of ADR = 20  $\mu$ s, AD = 5  $\mu$ s, and ADR =  $50 \mu s$ , AD =  $5 \mu s$ , respectively. The results are in



- Figure 11. Comparison of spatial profile of ionization obtained by time-integrated analysis and by time-scanned analysis, respectively. The signals by time-scanned analysis are normalized with respect to the signals by time-integrated analysis.
  - (.) denotes data processed by time-scanned analysis.
  - (o) denotes data processed by time-integrated analysis.

The analyte is 100  $\mu$ g/ml Na. Na<sup>+</sup> is produced by DLI with the dye laser tuned to the transition of the 3S<sub>k</sub> + 3P<sub>k</sub> level of sodium.

- Figure 12. The comparison of temporal profiles of ionization obtained by time-scanned analysis and by timeintegrated analysis, respectively.
  - (4): signal processed by time-scanned analysis; lifetime ( $\tau_1$ ) = 3.3 ± 0.3 µs.
  - (1) : signal processed by time-integrated analysis; aperture range = 20  $\mu$ s, aperture duration = 5  $\mu$ s;  $\tau_2$  = 3.2 ± 0.2  $\mu$ s.
  - ( $\phi$ ): signal processed by time-integrated analysis; aperture range = 50 µs, aperture duration = 5 µs;  $\tau_3$  = 3.6 ± 0.2 µs.
  - ( ): function of e<sup>-x</sup> used to compare to the other three curves.

The analyte is 100  $\mu$ g/ml Na. Na<sup>+</sup> is produced by DLI with the dye laser tuned to the transition of the 3S<sub>k</sub> + 3P<sub>3/2</sub> level of sodium.


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good agreement with the lifetime of  $3.3 \pm 0.3$   $\mu$ s obtained by time-scanned analysis.

#### B. Reagents

Solutions made from reagent grade sodium chloride and lithium chloride (Baker analyzed reagent, Phillipsburg, N.J.) were used to liberate free alkali metal atoms in the flame. The reasons that alkali metals were chosen in the DLI and LEI experiments are as follows:

(1) Because the ionization potentials of alkali elements are small (< 5.5 ev), they are sensitive to LEI by an N<sub>2</sub> laser-pumped dye laser although it is harder to obtain a detectable ionization signal than by a  $\mu$ s flashlamp-pumped dye laser, as described earlier in this chapter. In order to obtain some fundamental comparisons between DLI and LEI signals, it is useful to choose elements that are sensitive in the LEI technique.

(2) Alkali elements have been well characterized in flames and other hot vapors. Diffusion and mobility coefficients, collisional ionization cross sections, oscillator strengths and other parameters are known.

Rhodamine 6G, Rhodamine B, Rhodamine 101 and DCM were used as laser dyes. They were obtained from the Exciton Chemical Co. The first three laser dyes were

: ? prepared 5 x  $10^{-3}$  mole/l in ethanol solution; the concentration of DCM in DMSO was also 5 x  $10^{-3}$  mole/l. As the concentration of laser dye is changed, the profile of output power versus wavelength may shift significantly. By taking advantage of this property of the laser dye, a maximum output power in the desired wavelength region may be obtained.

# C. Procedure

The data reported here are mainly temporal profiles and spectral profiles of alkali ionization signals obtained by time-scanned analysis and single-point analysis. In order to obtain reliable data, precise system alignment is required prior to any data acquisition.

Briefly, the experimental procedure was as follows:

(1) After 10-20 minutes of warm-up time, the dye laser was first adjusted to maximum output power by slight adjustments of the optical components of the entire dye laser device. Detected by the joulemeter, the output power peak-to-peak stability were observed on the and oscilloscope. The calibration of laser wavelength and spectral profile (a Gaussian profile is expected) is made to the deflecting beam part of the by

monochromator-photomultiplier-strip chart recorder system.

(2) The burner head was fixed at the position where the dye laser beam and  $N_2$  laser beam from the opposite direction have maximum temporal overlap by examination with a photodiode set on the burner head.

(3) By moving a sheet of paper over the burner head, the focused beams of the dye laser and the N<sub>2</sub> laser were aligned to have a maximum overlap of their beam waists inside the inner flame.

(4) A pair of nichrome wires was mounted in the electrode holders, the position of the bottom probe was precisely set by moving a micrometer-driven translation stage. The two probes were suspended parallel to one another, separated by 4-10 mm, in the vicinity of the laser beams; the bottom probe was placed at a distance of about 10 mm above the burner head.

(5) The  $H_2-O_2$ -Ar flame was ignited and the salt solution was nebulized into the inner flame. It is important to follow the correct procedure to ignite the flame in order to prevent any danger. The Ar gas of the inner and mantle flames was first turned on by adjusting the flow meters. Then the  $H_2$  was sent through the flame system. The gaseous mixture of Ar and  $H_2$  was burned before turning on the  $O_2$  gas flow. Finally, the flow rate of each gas was adjusted to the appropriate setting on the flow meter. To turn off the flame, the reverse procedure was

followed

(6) An appropriate aperture delay range and aperture duration were selected to provide a reliable output with maximum signal-to-noise ratio.

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#### CHAPTER III

# EXPERIMENTAL AND THEORETICAL STUDIES OF DUAL LASER IONIZATION OF SODIUM IN AN H2-02-Ar FLAME

# A. Introduction

Laser-assisted ionization of gaseous atoms and molecules can yield detailed information about excited electronic states as well as provide an extremely sensitive method of analysis. Experimental techniques employed in the development of this field have included, for example, resonance ionization spectroscopy with a proportional counter for ion detection(22), and multiphoton ionization spectroscopy with detectors such as

electron multiplier thermionic diodes or mass spectrometers (64,99,123). Several theoretical models have been advanced which deal with the multiphoton and collisional steps involved in the process (124-129); perturbation theory and density matrix formalisms are often applied to the multiphoton ionization case.

Laser-assisted ionization has also been applied to

metal vapors in analytical flames, and results in a remarkable improvement in trace element sensitivity in many cases. This form of the optogalvanic effect has been termed laser-enhanced ionization (LEI) (2). In addition to being more sensitive than conventional flame fluorescence spectroscopy, LEI is free from such optical interferences as stray light, self-absorption, and flame background (7,130). However, the complex parameters of the flame gas composition, sampling system such as nebulizer efficiency, and free atomic fraction - all of which influence the ionization signal - make fundamental studies of ionization in a flame difficult. Accordingly, no theoretical treatment of LEI has been reported heretofore.

We have extended LEI of atoms in flames to include simultaneous irradiation by two different, collinear laser beams (131), a technique that we call dual laser ionization: DLI. The technique, described in section B, has been applied to alkali metal analytes, and we report here studies involving sodium solutions nebulized into a premixed  $H_2-O_2$ -Ar flame. We also introduce a theoretical model for the steps leading to ionization, and compare our experimental results to calculated predictions. In DLI multiphoton ionization can dominate over collisional ionization as the major analyte ionization process. In derive equaitons for section C we the multiphoton ionization rate - previously obtained by Geltman (124) by time-dependent perturbation theory - in matrix notation.

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The experimental results are reported and compared to those given by the theoretical model in section D. The discrepancies are attributed to inadequacies of the model when it is applied to partial saturation of the initial analyte excitation step. An empirical formula is proposed to reconcile the results, as discussed in section E.

#### **B.Experimental**

The experimental set-up for two-step, laser-assisted ionization in flames has been described in the previous chapter. Briefly, ions produced in the interaction region (1 cm above the Meker burner head) were collected by a pair of biased nichrome wire probes suspended parallel to one another, 1 cm apart, inside the flame. The probe current passed through a load resistor, and the resulting voltage was the input to a boxcar integrator (PARC Model 162 - 164). Signals were monitored oscilloscope (Model 564 Tektronix, with an Inc., Beaverton, OR), and the output was displayed on a strip chart recorder. A grating/filter double monochromator (Model Eu-701-30, GCA, Mcpherson ACTON, MA), followed by a photomultiplier module (Model Eu-701-30, GCA, Mcpherson), positioned at an angle of 90° to the incident beam, was used to measure fluorescence from the flame/laser

interaction region.

Rhodamine 6G was employed in the home-made Hansch-type dye laser, which was pumped by a 5 ns pulsed nitrogen laser (Model 0.5 - 150, NRG, Inc., Madison, WI). convex glass lens focused the tunable dye laser Α radiation onto a (1.0  $\pm$  0.3) x 10<sup>-3</sup> cm<sup>2</sup> area in the center of the flame. LEI was measured when the output of the dye laser was tuned to various resonances in the Na spectrum. For DLI measurements, a fraction of the N<sub>2</sub> pump laser output was reflected to the opposite side of the flame, and focused by a quartz lens onto a (2.0  $\pm$  0.4) x  $10^{-4}$  cm<sup>2</sup> area so that maximum overlap of the beam waists was effected. The optical elements were arranged to ensure that the two laser beams were also temporally coincident. A power meter (Model J3-05, Molectron Corp., Sunnyvale, CA) was used to measure the output power of the two lasers. Most data reported here were obtained with a dye laser power density of 50 MW/cm<sup>2</sup> and an  $N_2$  laser power density of 80 MW/cm<sup>2</sup>. The dye laser radiation was attenuated by insertion of neutral density filters between it and the flame. A set of calibrated filters was employed to vary the N<sub>2</sub> laser power density in a similar manner. In order to maintain constant conditions, the power density of each laser was checked frequently during the course of an experiment.

The flame gas consisted of  $H_2$ ,  $O_2$ , and Ar in selected proportion. The components were well mixed prior

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# C. Theoretical

# C-1 Multiphoton Ionization in a Two-level Atomic System

Multiphoton ionization is often treated in terms of time-dependent perturbation theory (77). We shall assume that this mechanism dominates the DLI process, and introduce matrix notation to develop an expression for the multiphoton ionization rate, analogous to Geltman's derivation (124).

In time-dependent perturbation theory, the

Hamiltonian H can be expressed semiclassically as

$$H = H^{O} + H_{int}$$
(1)

$$H_{int} = ZE\cos \omega t , \qquad (2)$$

where  $H^{O}$  is the unperturbed Hamiltonian of the atom,  $H_{int}$  represents interaction with the radiation field, Z is the atomic displacement, and E and  $\omega$  represent the amplitude and frequency of the field, respectively. We assume that the laser radiation is monochromatic and linearly polarized. The Schrödinger equation can then be written (fn = 1)

$$i\frac{\partial \Psi(\mathbf{r},t)}{\partial t} = (H^{\circ} + ZE \cos \omega t) \Psi(\mathbf{r},t)$$
(3)

The wavefunction can be expanded in terms of eigenfunctions,  $\phi_j(r)$  of the zeroth-order Hamiltonian (132), giving for a two-level system

$$\Psi(\mathbf{r},\mathbf{t}) = \sum_{j=1}^{2} a_{j}(\mathbf{t}) \Phi_{j}(\mathbf{r}) \exp[-i\varepsilon_{j}\mathbf{t}], \qquad (4)$$

where  $a_j(t)$  is a time-dependent coupling coefficient and  $\varepsilon_j$ is an eigenvalue of  $H^O$ . Substitution into the Schrödinger equation gives

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$$i\frac{da_{i}(t)}{dt} = \sum_{j=1}^{2} a_{j}(t) Z_{ij} E \cos \omega t \exp[i\omega_{ij}t], \quad (5)$$

where  $Z_{ij} = \langle \phi_i(r) | Z | \phi_j(r) \rangle$ , the dipole matrix element

between the unperturbed eigenfunctions, and  $\omega_{ij} = \omega_i - \omega_j$ , the energy difference between levels i and j. In matrix notation, Equation (5) can be written

$$i\frac{d}{dt} \begin{pmatrix} a_{1}(t) \\ a_{2}(t) \end{pmatrix} = \begin{pmatrix} 0 & Z_{12} \exp[i\omega_{12}t] \\ Z_{12} \exp[-i\omega_{12}t] & 0 \end{pmatrix}$$
$$x \begin{pmatrix} a_{1}(t) \\ a_{2}(t) \end{pmatrix} E \cos t \omega t .$$
(6)

One can define a matrix b as

$$b(t) = {\binom{b_1(t)}{b_2(t)}} = {\binom{\exp[in_1t] & 0}{0 & \exp[in_2t]}}$$
$$x {\binom{a_1(t)}{a_2(t)}},$$
(7)

where  $n_i$  is a function of the detuning energy.

Substitution of Equation (7) into Equation (6) followed by application of the rotational wave approximation (133,134) gives

$$i\frac{d}{dt}\binom{b_{1}(t)}{b_{2}(t)} = \frac{1}{2}\binom{-2n_{1}}{z_{12}E} \exp[i(\omega - \omega_{21})t] \exp[i(n_{1} - n_{2})t]}{z_{12}E} \exp[-i(\omega - \omega_{21})] \exp[-i(n_{1} - n_{2})t] - 2n_{2}}$$
$$x\binom{b_{1}(t)}{b_{2}(t)}.$$
(8)

We call the square matrix in Equation (8)  $\Omega$ , and introduce a matrix C to diagonalize it:

$$C^{-1}\Omega \quad C = \Lambda = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$
 (9)

Then from Equation (8)

$$b(t) = C \exp\left[\frac{-i\Lambda t}{2}\right] C^{-1} b(0)$$
 (10)

where we set the initial time equal to 0. Sustitution of Equation (10) into Equation (7) provides the solution to the coupled differential Equations (5).

# C-2 Application to Sodium

# Consider the case:

Na  $(3S_{\frac{1}{2}}) + \hbar\omega_{1} + Na (3P_{3/2}) + \hbar\omega_{2} (or + 2h\omega_{1}) + Na^{+} + e^{-}$ . When the dye laser (with energy  $\hbar\omega_{1}$ ) is tuned across the  $3S_{1/2} + 3P_{3/2}$  transition a ground-state sodium atom may absorb a photon and reach the  $3P_{3/2}$  level; subsequent absorption of a photon from the  $N_{2}$  laser ( $h\omega_{2}$ ) provides sufficient energy to reach the ionization continuum. We treat this case as a two-level atomic system, neglecting coupling between the  $3P_{3/2}$  and  $3P_{1/2}$  levels. Then  $n_{1} = 0$ , and setting  $n_{2} = \omega - \omega_{21} \equiv \Delta$  we find

$$\Omega = \begin{pmatrix} 0 & z_{12}E_1 \\ z_{12}E_1 & -2\Delta \end{pmatrix}.$$
(11)

By setting the secular determinant of  $\Omega$  equal to zero we obtain the diagonal matrix  $\Lambda$ ,

$$\Lambda = \begin{pmatrix} -\Delta + [\Delta^{2} + z_{12}^{2}E_{1}^{2}]^{\frac{1}{2}} \\ 0 & -\Delta - [\Delta^{2} + z_{12}^{2}E_{1}^{2}]^{\frac{1}{2}} \end{pmatrix}.$$
(12)

From Equations (9) and (12), the transform matrix C is found

$$C = \begin{pmatrix} 1 & \Omega_{12}/\lambda_{2} \\ \lambda_{1}/\Omega_{12} & 1 \end{pmatrix} , \qquad (13)$$

where  $\Omega_{12} = Z_{12}E_1$  and  $\lambda_{1,2} = -\Delta \pm [\Delta^2 + Z_{12}^2 E_1^2]^{\frac{1}{2}}$ .

Substitution of Equations (12) and (13) into Equation (10) and application of the initial condition,  $b_1(0) = \delta_{i1}$  gives

$$b = B \begin{pmatrix} \exp[-i\lambda_1 t/2] \\ \exp[-i\lambda_2 t/2] \end{pmatrix}$$
(14)

where

$$B = \frac{\lambda_{2}}{\lambda_{2} - \lambda_{1}} \begin{pmatrix} 1 & -\lambda_{1}/\lambda_{2} \\ -\lambda_{1}/\Omega_{12} & \lambda_{1}/\Omega_{12} \end{pmatrix}$$
$$= \frac{1}{2(\Delta^{2} + \Omega_{12}^{2})^{\frac{1}{2}}} \begin{pmatrix} \Delta + (\Delta^{2} + \Omega_{12}^{2})^{\frac{1}{2}} & -\Delta + (\Delta^{2} + \Omega_{12}^{2})^{\frac{1}{2}} \\ \Omega_{12} & \Omega_{12} \end{pmatrix}$$
(15)

The related transition probability can be expressed as

$$P = \sum_{j=1}^{2} |B_{2j}|^2 = \frac{\alpha_{12}^2}{2(\Delta^2 + \alpha_{12}^2)} .$$
 (16)

If the two laser beams are linearly polarized and parallel, we obtain for the rate of multiphoton ioization induced by simultaneous absorption

$$W = \sum_{j=1}^{2} |B_{2j}|^{2} \left( \frac{1}{4E_{1}^{4}} \sum_{f} |S_{2k}|^{2} + E_{2}^{2} \sum_{f} |Z_{2k}|^{2} \right), \quad (17)$$

where

$$S_{2k} = \sum_{\ell} Z_{2\ell} Z_{\ell k} / (\omega_{\ell 2} - \omega)$$
(18)

In Equation (17)  $E_1$  and  $E_2$  are the electric fields of the dye laser and the N<sub>2</sub> laser, respectively.  $Z_{2k}$  is the first-order dipole matrix element for the transition from the  $3P_{3/2}$  level to continuum level k, where k is the kquantum number of an allowed continuum state; since  $|2\rangle =$  $|3B_{3/2}\rangle$ , k can be  $kd_{3/2}$ ,  $kd_{5/2}$  or  $kf_{5/2}$  for linearly polarized radiation (77).  $S_{2k}$  is a matrix element of the second order solution, since two additional dye photons are required to promote sodium from  $|2\rangle$  to the continuum. The first term of Equation (17) represents three-(dye) photon ionization; i.e. it covers  $Na(3S_{1/2}) + 7w_1 \rightarrow$  $Na(3P_{3/2}) + 2hw_1 \rightarrow Na^+ + e^-$ , the multiphoton case of LEI,

ieç. 102 ile. :::e :.s; tte :203 ::e 199 I calo • • lteo fito 2251 ,e • lià £555 39 ilook  neglecting, however, the contribution of collisional ionization. The second term covers additional ionization due to DLI, again ignoring collisional contributions to the ionization rate.

calculations, matrix elements for In our discrete-to-discrete state transitions are estimated on the basis of the Bates-Damgaard approximation (135), and those for discrete-continuum transitions are obtained by the quantum defect method (100). The same treatment was applied by Geltman (124). We have repeated one case calculated in reference (124), Na( $3S_{1/2}$ ) + 2ħ $\omega$  + Na( $5S_{1/2}$ ) +  $\hbar_{\omega}$  +  $Na^+$  +  $e^-$ , and obtained very good agreement. Theoretical calculations of the ionization rate as a function of the detuning energy have been performed on the basis of Equation (17) for two cases:

(a) DLI (ignoring the negligible contribution from the E<sub>1</sub> term under these conditions) : Na(3S<sub>1</sub>) +  $\hbar \omega_1$ (589 nm)  $\rightarrow$  Na(3P<sub>3/2</sub>) +  $\hbar \omega_2$ (337 nm)  $\rightarrow$  Na<sup>+</sup> + e<sup>-</sup>

(b)LEI (where the  $E_2$  term in the equation is absent) : Na(3S<sub>1</sub>) +  $\hbar\omega_1$ (589 nm) + Na(3P<sub>3/2</sub>) +  $2\hbar\omega_1$ (589 nm) + Na<sup>+</sup> + e<sup>-</sup>

The results are shown in Figures 13 and 14, respectively. We omit treatment of the case:  $Na(3S_{1/2}) + 2h \omega_2(337 \text{ nm}) + Na^+ + e^-$ , since no detectable signal was experimentally observed when the dye laser beam was blocked. The experimental and calculated results will be compared in the next section.



Calculated fontration Forte (51)



 $\begin{array}{l} \rightarrow \text{ Na' + e}; \\ \text{a) } P_{\text{dye}} = 50 \text{ MW/cm}^2; \text{ b) } P_{\text{dye}} = 5 \text{ MW/cm}^2; \\ \text{c) } P_{\text{dye}} = 0.5 \text{ MW/cm}^2. \end{array}$ 

# D. Results

#### D-1 Multiphoton Ionization in the Flame

Enhanced ionization of sodium in the flame under the influence of the dye laser alone (LEI) could occur through resonance absorption to the  $3P_{3/2}$  state, followed by interactions with two additional photons as required to reach the ionization continuum ( case (b) above ). The LEI signal was measured as the dye laser power was attenuated by an order of magnitude. The power dependence is shown logarithmically in Figure 15, where a slope equal to one is obtained. Thus three-photon ionization is not the predominant mechanism for LEI under our conditions. Rather, collisions between the resonantly excited sodium atoms and the other components of the flame gas must provide the energy necessary for ionization. Indeed, collisional interactions among the components have been invoked previously to account for both conventional and laser-induced ionization in flames (4,136).

As noted in our previous paper (131), when the N<sub>2</sub> laser beam is permitted to impinge on a flame already under  $3S_{1/2}^+$   $3P_{3/2}$  resonance excitation by the dye laser, the ionization signal increases by about two orders of





magnitude. The dependence of the DLI signal on the N<sub>2</sub> laser power is shown in Figure 16; it is linear over almost two decades of laser power. (The fall-off at high power levels is probably due to partial saturation.) This result indicates that DLI occurs by a multiphoton pathway, case (a) above.

The ratio of ionization signals from DLI and LEI depends strongly on the wavelength of the dye laser beam. It is plotted as a function of detuning wavelength in Figure 17. The maximum DLI enhancement is obtained at the resonance wavelength, and the ratio drops quickly on either side. This observation may be understood in terms of resonant multiphoton ionization (81), where the relatively long lifetime of the intermediate stationary state (v17 nsec for the 3P state of Na (121)) facilitates absorption of an additional photon after the initial excitation. The corresponding lifetimes of the virtual involved intermediates in states as non-resonant multiphoton absorption are on the order of  $10^{-15}$  sec. in Figure 17 can be Alternatively, the results shown interpreted in terms of the total, generalized two-photon cross section, which is larger at the resonance wavelength than off-resonance.



N2 laser power dependence measurement of DLI, with constant dye laser power (arbitrary units). The line has a slope = 1, throughout most of the power range, except at high power.



and LEI signals were measured alternately as the Enhancement ratio of DLI to LEI versus detuning wavelength. Resonance wavelength = 5890 Å. DLI dye laser was tuned across the  $3S_1 + 3P_3/2$  transition.

D-2 Measurement of the Dye Laser Profile by DLI

The spectral profile of laser-induced atomic fluorescence in a flame involves a convolution of the laser and atomic profiles (137). Since the full width at half-maximum (FWHM) of a broad-band dye laser is much larger than that of an atomic line, the resulting fluorescence profile can be taken as a measure of the laser profile. The DLI signal across the  $3S_{1/2} \rightarrow 3P_{3/2}$ resonance was monitored as a function of dye laser power. The FWHM dropped from about 0.8 Å at high power to a constant value of 0.5 Å at powers below 0.5 MW/cm<sup>2</sup>. The normalized DLI profile is shown in Figure 18, where it is compared with the profile obtained by measuring the  $3P_{3/2}$ +  $3S_{1/2}$  fluorescence under the same experimental conditions. The results are essentially coincident; the minor deviations may be caused by the small error in determining the resonant wavelength. Thus the FWHM of the ionization profile in the flame is also limited by the dye laser. Similar conclusions have been drawn for low-density vapor cell systems (138,139).



# D-3 Dependence of the Ionization Profile on Dye Laser Power

The breadth of the ionization profile from DLI in the flame may depend on many factors: laser power, sodium concentration, flame gas composition, configuration of the beams, probe voltage, geometry of the two laser interaction zone in relation to the probe electrodes, etc. Consequently it is difficult to make a quantitative investigation of an individual ionization profile in the flame, with which to compare the results of theoretical calculations. However, noteworthy changes are observed in the DLI profile when the dye laser power is altered, which we attribute to this parameter, alone. These are depicted in Figure 19, where the integrated signal from the boxcar averager (in arbitrary units) is plotted versus the detuning energy for dye laser powers of 50, 5 and 0.5 MW/cm<sup>2</sup>. Relative ion populations may be obtained from ratios of such ionization profiles. Multiphoton ionization rates, which are linearly proportional to the ion populations (140), may be calculated via the formalism section С. Experimentally determined outlined in ionization ratios are compared with predicted values, calculated according to Equation (17), in Figure 20. The deviation is significant.

An implicit assumption of the model upon which the

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calculated ionization rate ratios is based is that the intermediate state resonantly excited in the first step of multiphoton mechanism is saturated. Under such the conditions, the DLI signal would be independent of the dye laser power. The actual relationship under our experimental conditions is shown in Figure 21. Over much of the power range of a slope of about 0.5 is obtained. Complete saturation is not observed, even at the maximum powers available. Thus the deviations between the experimental and calcualted ionization profile ratios depicted in Figure 20 may not reflect fundamental inadequacies in the theory.

## E. Discussion

The model employed here is based on a saturated excited state. Equation (16), which describes the transition probability for an excited state, becomes independent of the dye laser power as the resonance wavelength is reached (i.e.  $\Delta = 0$ ). Lambropolous (129) used time-dependent perturbation theory to treat a two-photon resonant ionization case. He pointed out that the ionization rate is linearly proportional to the light intensity when the intensity is such that stimulated deexcitation of the exicted state is much more probable

Figure 21. Dependence of DLI on the dye laser power. DLI is induced by the dye laser tuned to the Na  $3S_{\frac{1}{2}}$  $\rightarrow 3P_{3/2}$  transition, followed by absorption of a photon from the N<sub>2</sub> laser. • indicates experimental results; the solid line (slope = 0.5) is obtained from an empirical formula [Equation (20)]. Arbitrary units are used for both axes.



than spontaneous decay; otherwise, for much lower intensity, the rate would be proportional to the square of the intensity. These two models, based on time-dependent perturbation theory, can be applicable either to a saturated or to an unsaturated excited state.

As shown in Figure 22, a log-log plot of the laser-induced fluorescence (LIF) from the 3P level as a function of dye laser intensity also gives a slope of 0.5. Clearly, the resonance transition is only partially saturated. Measurements of the ionization signal produced by subsequent absorption of  $N_2$  laser photons as a function of dye laser power also yielded a slope  $\sim 0.5$  over two decades as shown in Figure 21. Moreover, when the lens employed to focus the dye laser beam in the flame is removed the log-log dependence of the  $3P_{1/2} + 3S_{1/2}$  LIF (dual beam conditions) on the dye laser power had a slope of  $\sim$  0.8, as shown in Figure 23. Under these conditions the excited state population is essentially unsaturated, and a log-log plot of the DLI signal as a function of dye laser power (Figure 24) gives a slope of  $\sim 1$ . The DLI multiphoton ionization signal is proportional to the transition probabiltity to the excited state.

LIF intensity induced by one laser and two lasers (Figure 22) is comparable. However, the ionization intensity of DLI is about two order of magnitude greater than that of LEI. Under our experimental conditions, the  $3P_{3/2}$  state of Na is only partially saturated; this



Egure 22. Dependence of LIF on the dye laser power( arbitrary units ). LIF is monitored from the  $3P_{3/2} + 3S_{\frac{1}{2}}$ transition of Na, following resonance excitation. Na concentration = 100 ppm. $\triangle$  indicates LIF with the dye laser alone; o indicates LIF with dual lasers. The slope for both lines is  $\sim 0.5$ .



Figure 23. Dependence of LIF on dye laser power (arbitrary units). LIF is monitored from the  $3P_{1_2} \rightarrow 3S_{1_2}$  transition of Na, following excitation from the  $3S_{1_2} \rightarrow 3P_{3/2}$  level. Na concentration = 10 ppm.  $\land$  indicates no lens used to focus the dye laser beam prior to the flame; the slope of the line  $\sim 0.8$   $\circ$  indicates a lens used to focus the dye laser beam into the flame; the slope of the line  $\sim 0.5$ .



Figure 24. Dependence of DLI on dye laser power (arbitrary units). The dye laser is tuned to resonance with the  $3S_{\frac{1}{2}} \rightarrow 3P_{3/2}$  transition. No lens is used to focus the dye laser beam into the flame. The slope = 1.0 ( Compare Figure 9, where a lens was employed ).

results in "unsaturated" LEI (Figure 15), because weak collisional coupling links the excited state and the ionization continuum. In DLI, however, the strong radiation field of the N<sub>2</sub> laser couples the selected excited state and the continuum, resulting in an enhanced ion signal.

Gontier and Trahin (84) have pointed out that the slope of the power dependence of ionization is a function laser intensity and laser pulse duration. Their of predictions agree very well with the experimental results obtained with different laser intensities and pulse durations for a three-photon absorption/four-photon ionization of cesium. Among these results were a slope of 4 with 15 ps and  $10^9$  W/cm<sup>2</sup> (141), a slope of 2.5 with 40 ns and  $4 \times 10^7$  W/cm<sup>2</sup> (142), and a slope of 2 with 10 nsec and  $2 \times 10^9$  W/cm<sup>2</sup> (143). Obviously, the slope is not simply determined by laser intensity alone. These experiments show a tendency for partial saturation and demonstrate the influence of the temporal effect, when compared to the predicted slope of 4 for standard photon numbers involved in four photon - three photon а resonant-ionization case. These phenomena cannot be simply interpreted by a model based on perturbation theory. The applicable domain of models based on perturbation techniques has been theoretically examined by Beers and Armstrong, who presented an exact solution to a realistic

model for resonant two-photon ionization (144).

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An examination of the partial saturation of LIF under our DLI conditions helps to interpret the deviation from Geltman's model. An attempt is made to modify Equation (16) empirically so that :

$$P = K E_{1} \sum_{j=1}^{2} |B_{2j}|^{2}$$

$$= K E_{1} \Omega_{12}^{2} / 2(\Delta^{2} + \Omega_{12}^{2}) .$$
(19)

In this equation the transition probability is chosen to be proportional to the square root of the dye laser power. This particular power dependence was selected to provide the same slope as that obtained for LIF (in Figure 22). Coefficient K in Equation (19) provides correct units. The modification of Equation (19) is an empirical one, and has not been justified mathematically. Substitution into Equation (18) yields the empirical rate of multiphoton ionization, W':

$$W' = K E_{1} \sum_{j=1}^{2} |B_{2j}|^{2} \left( \frac{1}{4E_{1}} \sum_{f} |S_{2k}|^{2} + E_{2}^{2} \sum_{f'} |Z_{2k}|^{2} \right).$$
(20)

Based on Equation (20), a slope = 0.5 is expected for the dye laser power dependence of DLI. A line with slope = 0.5 is included with the experimental results in Figure 21. The agreement with experimental results is over two decades of power density. Two laser powers, 5.0 MW/cm<sup>2</sup> and 2.4 MW/cm<sup>2</sup>, were selected from the coincident segment, and the ratio of the DLI signals for these two powers was

calculated as a function of the detuning energy. Results of the calculation agree well with experimental results, as is shown in Figure 25.

The resonant photoionization rate of DLI, assuming saturation of the  $3P_{3/2}$  state of Na and  $P_{N_2} = 80 \text{ MW/cm}^2$ , is estimated from Equation (17) to be 6.5 x 10  $8 \text{ s}^{-1}$ . Aymar et al.(145) have calculated the photoionization cross section from the  $3P_{3/2}$  state to the continuum ( $\epsilon = 0.014$  Rydberg) to be 3.5 x  $10^{-18}$  cm<sup>2</sup> by the parametric potential method. Under irradiation of 80 MW/cm<sup>2</sup> (the N<sub>2</sub> laser power in our case), the photoionization rate is calculated to be 8.6 x  $10^8 \text{ s}^{-1}$ , which agrees satisfactorily with the estimation from Equation (17).

For the experimental conditions,  $P_{dve} = 50 \text{ MW/cm}^2$ and  $P_{N_{2}} = 80 \text{ MW/cm}^{2}$ , the calculated (Equation (17)) ionization enhancement of DLI over LEI is about seven orders of magnitude (Compare Figure 13 and 14). The observed enhancement is only about two orders of magnitude, which demonstrates that collisions -- which are ignored in the developement outlined in this chapter -make a significant contribution to ionization in LEI. Indeed, the dependence of LEI on the dye laser power (Figure 15) shows that collisions dominate the ionization mechanism following  $3S_{1/2} \rightarrow 3P_{3/2}$  resonant excitation. The collisional factor is considered explicitly in the next chapter; this leads to a much improved comparison of expected and observed DLI/LEI enhancement factors.





#### F. Conclusion

The ionization mechanisms of sodium DLI and LEI following resonant excitation to the  $3P_{3/2}$  state have been examined in this chapter, including the relationship of the ionization profile (DLI signal vs. detuning wavelength) to the laser profile and the influence of detuning on the DLI/LEI enhancement ratio. Geltman's theoretical model (124), which presumes saturation of the intermediate state, was recast in matrix notation and used to help interpret the observed ionization profiles. The DLI photoionization rate calculated from the theoretical model agrees satisfactorily with that produced by other authors.

LIF measurements demonstrate that the  $3P_{3/2}$  state is only partially saturated under our experimental conditions, and when comparison with experimental results is made, significant deviations from the predications of the theoretical model are observed. The model does provide quite satisfactory agreement, however, when the empirical dependence on the power of the laser used for resonance excitation is included. The DLI/LEI enhancement ratio is severely overestimated by the multiphoton ionization mechanisms considered in this chapter. Collisional processes cannot be ignored. They are included in the rate equation treatment of DLI and LEI in the next chapter, and an improved enhancement ratio prediction results. A more general assessment of energy level schemes, and conditions under which DLI possesses advantages for trace metal analysis, is given in Chapter VII.

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#### CHAPTER IV

# RATE EQUATION APPROACH TO A THREE-LEVEL SYSTEM FOR DUAL LASER IONIZATION AND LASER-ENHANCED IONIZATION

#### A. INTRODUCTION

Laser-enhanced ionization (LEI) in flames has a sensitive trace metal recently been developed as analysis technique (2-4,18). Briefly, in LEI a laser is tuned to resonance with an absorption line of an atomic species, thus promoting some atoms to an excited electronic state. Because the ionization energy of an excited atom is lower than that for ground state atoms, it becomes more feasible to ionize these excited atoms via collisional photoionization-dominated processes. or Typically, ionization in single laser LEI is dominated by collisions (2.4). In contrast, LEI with two lasers, which we call dual laser ionization (DLI), may be а multiphoton-dominated ionization process (131,146). The DLI technique employs an apparatus analogous to the LEI technique, except that two lasers are used: one is an  $N_2$ laser-pumped dye laser and the other is the  $N_2$  pumping laser. Both lasers are directed collinearly into the same

area inside an  $H_2-O_2$ -Ar flame, with maximum spatial and temporal coincidence above the burner head. A pair of biased nichrome wires, suspended parallel to each other inside the flame, collects the ions of the analyte, which is nebulized into the flame. The resulting probe current is converted into a voltage, and the signal is processed by a boxcar integrator; a readout system is employed to record the ion signals (131, 146). The competition between photoionization and collisional ionization processes is affected by the energy defect between the analyte excited state produced by the laser and it continuum threshold (2). The collisional ionization rate increases nearly exponentially with decreasing energy defect, based on simple Boltzmann theory (147).

Herein, a rate equation formulation is used to describe the impact on and the relationship between DLI and LEI under various conditions. Rate equation have been widely used to model atomic formulations excitation phenomena with lasers or other sources because of their simplicity (148-152). More exact treatment of the interaction between atoms and light must be made by the density matrix formulation or more elaborate atomic operators. Ackerhalt and Eberly have examined the validity of rate equations applied in the case of resonant multilaser ionization (153). Daily used rate equations to describe laser excitation in flames (154).Common conclusions were reached. Under appropriate conditions,

the rate equation formulation in dealing with an N-level system of the analyte only requires N equations, instead of nearly  $N^2$  equations adopted in the density matrix formulation. The difference occurs because of the neglect of "off-diagonal" terms in the rate equations. This approach is appropriate for the processes in which the population changes monotonically. If the atom is subjected to intense, coherent, nearly resonant radiation, pulsations of level populations may occur (153,155). Winefordner and coworkers pointed out that the conditions for using rate equations to describe laser excitation in atmospheric pressure flames are generally fulfilled for laser rise times of the order of 1 nsec or more (149).

In addition to examining briefly the validity of the rate equation formulation for our system, this chapter attempts to better describe the relationship between ionization and fluorescence induced by DLI and LEI, and to compare various characteristics of DLI with LEI.

### B. Theoretical Basis

#### B-1. General Solution

A three-level system showing rate processes for LEI and DLI is illustrated in Figure 26. The addition of the



ionization cross section from the excited state is very small, and is considered negligible here. The symbols Figure 26. Three-level energy diagrams for (a) LEI and (b) DLI. The scheme is restricted to specific excited states photons to reach the continuum. The two-photon are defined in the text.

). Di Ili phot the lase that tay CORS 011 This pres the that áen s lini thro the Rigu 200.s ab so Plot ಯಾಗ lase sçec pumping N<sub>2</sub> laser in the DLI technique introduces the photoionization rate constant R in Figure 26b, which is only difference between the two models. the The laser-assisted collisional system studied by George showed that the interaction between laser radiation and particles may lead to a change in the collisional ionization rate constant; i.e. the effects of laser radiation and collisions are not independent of one another (156,157). This possible perturbation is neglected in the models presented here. Prior to reaching a general solution of the system, several assumptions must be made:

1. No coherent effect is produced in the system, so that the rate equations can be safely used instead of the density matrix formulation. We shall estimate the limitation imposed by this assumption in Section C.

2. The cross section for two-photon ionization through virtual states is very small in comparison with the cross sections of the other processes present in Figure 26. Therefore, we neglect the radiative rate constant from state 2 to the continuum caused by absorption of two additional dye laser photons, and the photoionization rate constant from the ground state to the continuum caused by absorption of two photons from the N<sub>2</sub> laser. (This assumption is made in dealing with the special cases of Na (3S + 3P) in Section B-2).

3. The rate constants applicable to LEI are not disturbed by the addition of the  $N_2$  laser used in DLI.

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4. The laser radiation density is spatially homogeneous.

5. The population distribution in states other than the three states considered in the models is neglected.

Based on the scheme shown in Figure 26, a set of rate equations for the LEI case can be written:

$$\frac{dn_i}{dt} = k_{2i}n_2 - Kn_i$$
(1)

$$\frac{dn_2}{dt} = B_{12}Un_1 + Kn_i - (B_{21}U + A_{21} + k_{21} + k_{2i})n_2$$
(2)

$$\frac{dn_1}{dt} = (B_{21}U + A_{21} + k_{21})n_2 - B_{12}Un_1$$
(3)

$$1 = n_1 + n_2 + n_1 (4)$$

For simplicity, the population densities  $n_1$ ,  $n_2$  and  $n_i$  above are taken relative to the total population density  $n_T$ . But for clarity  $n_i/n_T$  and  $n_2/n_T$  are used in the figures instead of  $n_i$  and  $n_2$ , respectively. The other symbols used in Equations (1-4) are  $k_{ij}$  (s<sup>-1</sup>), the collisional rate constant from state i upward to state j or deexcitation rate constant from i state downward to j state; K (s<sup>-1</sup>), the relaxation rate constant, as a sum of radiative, radiationless and recombination rate constants monitored from the continuum;  $B_{ij}(cm^2Hz/Wsec)$ , the Einstein absorption or stimulated emission coefficient;  $A_{21}(s^{-1})$ , the Einstein spontaneous emission coefficient and U (W/cm<sup>2</sup>Hz), the spectral irradiance of the laser.

Substitution of Equation (4) into Equation (2)

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yields

where

$$\frac{dn_2}{dt} = B_{12}U + (K - B_{12}U)n_i - (B_{12}gU + Z)n_2, \quad (5)$$

 $g = 1 + \frac{g_1}{g_2}$ 

$$g_2$$
 (6)  
 $Z = A_{21} + k_{21} + k_{2i}$ . (7)

If the system is in thermodynamic equilibrium, the relation between  $B_{12}$  and  $B_{21}$  is  $B_{12}g_1=B_{21}g_2$  (158);  $g_i$  is the statistical weight of the ith state. In the following we divide the discussion into several cases, including the steady state  $(dn_2/dt \simeq 0)$  case, and the nonsteady state case, with laser profiles that are step functions or rectangular pulse functions.

(a) Steady State with  $dn_2/dt \sim 0$ 

Under steady state conditions, Equation (5) yields

$$n_{2} = \frac{B_{12}U + (K - B_{12}U)n_{i}}{B_{12}gU + Z}$$
(8)

The spectral irradiance U(t) is assumed to be a unit step function

$$U = \begin{cases} 0 & t < 0 \\ U_{\circ} & t \ge 0 \\ & & & & & \\ \end{cases}$$
(9)

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If Equation (6) and (7) and the boundary condition:  $n_i(0) = 0$ , are substituted into Equation (1), the solution  $n_i(t)$  of the first order differential equation yields

$$n_{i}(t) = \frac{N}{M} (1 - e^{-Mt})$$
, (10)

where

$$M = K - \frac{k_{2i}(K - B_{12}U_{\circ})}{B_{12}gU_{\circ} + Z}, \qquad (11)$$

and

$$N = \frac{k_{2i}^{B} 12^{U_{\circ}}}{B_{12}^{g} U_{\circ} + Z}$$
(12)

Equation (10) describes the temporal behavior of the ion population density under steady state conditions. We shall discuss the validity to the laser pulse duration in using the steady state approximation to describe the ion behavior.

Typically, a boxcar integrator is experimentally employed to process the signals generated by a pulsed laser. For simplicity, we consider the gain factor to be unity and assume the gate function in a boxcar is

$$b = \begin{cases} 1 & 0 \le t \le T \\ 0 & \text{elsewhere} \end{cases}$$
(13)

Multiplying the gate function b by  $n_{i}(t)$  and dividing the

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integrated result by the aperture duration T yields the averaged population density  $\overline{n}_i$  as follows:

$$\overline{n}_{i} = \frac{1}{T} \left[ \int_{\circ}^{T} n_{i}(t) dt \right]$$
(14)

Substitution of  $n_i$  (t) in Equation (10) into Equation (14) gives

$$\overline{n}_{i} = \frac{N}{M} + \frac{1}{T} \left[ \frac{N}{M^{2}} (e^{-MT} - 1) \right]$$
(15)

# (b) Nonsteady State (Analytical) Solution

As long as a short laser pulse is employed, nonsteady state conditions should be considered because the laser pulse duration is not long enough for a steady state population to be reached. It is not difficult to obtain the analytical solutions for  $n_i(t)$  and  $n_2(t)$  from Equations (1-4). A complete solution of the coupled differential equations gives:

$$n_{i}(t) = C_{1}e^{-\epsilon_{1}t} + C_{2}e^{-\epsilon_{2}t} + n_{ip}$$
(16)  
$$n_{2}(t) = C_{3}e^{-\epsilon_{1}t} + C_{4}e^{-\epsilon_{2}t} + n_{2p} ,$$

where

$$\varepsilon_{1,2} = \frac{1}{2} \{ (K + B_{12}gU + Z) = 1 \}$$

 $\sqrt{(K + B_{12}gU + Z)^2 - 4[K(K + B_{12}gU + Z) - k_{2i}(K - B_{12}U)]}$  (17) n<sub>ip</sub> and n<sub>2p</sub> indicate the particular solutions of Equations (1) and (2), respectively. The results are

$$n_{ip} = \frac{B_{12}Uk_{2i}}{\epsilon_{1}\epsilon_{2}}$$

$$n_{ip} = \frac{B_{12}UK}{\epsilon_{1}\epsilon_{2}}$$
(18)

The coefficients  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  are not linearly independent of one another, because  $n_1$  and  $n_2$  are coupled to each other in Equations (1-2). By substituting Equation (16) into either Equation (1) or Equation (2), one obtains

$$C_{3} = \frac{K - \epsilon_{1}}{k_{2i}} C_{1}$$

$$C_{4} = \frac{K - \epsilon_{2}}{k_{2i}} C_{2}$$
(19)

The values of  $C_1$  and  $C_2$  can be obtained by applying the boundary conditions:  $n(0) = n_{10}$  and  $n_2(0) = n_{20}$  to Equation (16). That leads to

$$n_{i0} = C_{1} + C_{2} + n_{ip}$$
(20)  
$$n_{20} = \left(\frac{K - \epsilon_{1}}{k_{2i}}\right) C_{1} + \left(\frac{K - \epsilon_{2}}{k_{2i}}\right) C_{2} + n_{2p}$$

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The solutions for  $C_1$  and  $C_2$  are:

$$C_{1} = X \left( \frac{K - \varepsilon_{2}}{\varepsilon_{1} - \varepsilon_{2}} \right) - Y \left( \frac{k_{2i}}{\varepsilon_{1} - \varepsilon_{2}} \right)$$

$$C_{2} = Y \left( \frac{k_{2i}}{\varepsilon_{1} - \varepsilon_{2}} \right) - X \left( \frac{K - \varepsilon_{1}}{\varepsilon_{1} - \varepsilon_{2}} \right)$$
(21)

where

$$X = n_0 - n_{ip}$$
(22)  
$$Y = n_{20} - n_{2p}$$

At t = 0, the initial population densities  $n_{i0}$  and  $n_{20}$  of the continuum and the excited state can be obtaind by solving Equations (1-2) with the steady state assumption (without spectral irradiation (11)). The results are:

$$n_{10} = \frac{k_{21}k_{12}}{K(k_{12} + k_{21} + k_{21}) + k_{21}(k_{12} - K)}$$

$$n_{20} = \frac{Kk_{12}}{K(k_{12} + k_{21} + k_{21}) + k_{21}(k_{12} - K)}$$
(23)

Equation (16) describes the temporal behavior of the population density of the continuum and excited state, respectively. Similarly, the averaged population densities  $\overline{n}_i$  and  $\overline{n}_2$  processed by the boxcar integrator can be obtained according to Equation (14).

#### (c) Rectangular Function for Spectral Irradiance

Here we assume the spectral irradiance U is a rectangular function:

$$U = \begin{cases} U_{\circ} & 0 \leq t \leq T \\ 0 & \text{elsewhere} \end{cases}$$
(24)

Although the rise time of the laser profile is never equal to zero, the rectangular function assumption is closer to the experimental conditions observed with pulsed laser radiation than in the unit step function assumption. As the laser is turned on, the resulting population density for a specific level is the same as that discussed in cases (a) and (b) above. The laser irradiiates the system for T sec., then its spectral irradiance falls to zero. Consequently, the population dnesity has a different distribution after T sec from that with spectral irradiance U.

For the steady state case (a), the temporal behavior of the relative ion population density at times larger than T follows

$$n_{i}(t) = n_{iT} \exp[(\frac{k_{2i}K}{Z} - K)(T - t)],$$
 (25)

where  $n_{iT}$  indicates the population density at time T, and t is the time after the spectral irradiance falls to zero. For the nonsteady state case (b), by solving Equations (1-4) without spectral irradiance, one obtains

$$n_{i}(t) = c_{1}' e^{-\epsilon_{1}'t} + c_{2}' e^{-\epsilon_{2}'t}$$

$$n_{2}(t) = c_{3}' e^{-\epsilon_{1}'t} + c_{4}' e^{-\epsilon_{2}'t}$$
(26)

where

$$\varepsilon_{1,2} = \frac{1}{2} [(K+Z) \mp \sqrt{(K+Z)^2 + 4(Kk_{2i} - KZ)}]$$
 (27)

and

$$C'_{3} = \frac{K - \epsilon'_{1}}{k_{2i}} C'_{1}$$

$$C'_{4} = \frac{K - \epsilon'_{2}}{k_{2i}} C'_{2}$$
(28)

Equation (26) are analogous to those obtained in Equation (16); they describe the temporal behavior of  $n_i$  and  $n_2$  after the laser is off. The coefficients C'<sub>1</sub> and C'<sub>2</sub> can be obtained by applying the boundary conditions  $n_i(T) = n_{iT}$  and  $n_2(T) = n_{2T}$  to Equation (26). The results are:

$$c'_{1} = \left[ \begin{array}{c} n_{iT} \left( \frac{K - \epsilon'_{2}}{k_{2i}} \right) - n_{2T} \right] \frac{k_{2i}}{(\epsilon'_{1} - \epsilon'_{2}) \exp(-\epsilon'_{1}T)} \\ c'_{2} = \left[ \begin{array}{c} n_{2T} - \left( \frac{K - \epsilon'_{1}}{k_{2i}} \right) n_{iT} \right] \frac{k_{2i}}{(\epsilon'_{1} - \epsilon'_{2}) \exp(-\epsilon'_{2}T)} \\ \end{array} \right]$$
(29)

For convenience, we take the same period of time

for both the laser spectral irradiance and the boxcar gate function to obtain the averaged population density; i.e. if the rectangular spectral irradiance pulse is  $5 \times 10^{-9}$  sec long, the aperture duration of the boxcar is also  $5 \times 10^{-9}$ sec. We shall compare the effects of laser pulse duration on both DLI and LEI in Section C on this basis. The equations derived above are suitable for the LEI system. As mentioned previously, the difference between the DLI and LEI schemes in Figure 26 is that a photoionization rate constant R, a function of the N<sub>2</sub> laser power, is added to the former. Hence, by using R + k<sub>2i</sub> instead of k<sub>2i</sub>, we may still use the related equations in the above cases to describe the DLI system.

## B-2 Special Case

Because the sensitivities of DLI and LEI have been compared for sodium (131), we use sodium here as an example. The sodium atoms in the premixed  $H_2-O_2$ -Ar flame are first excited to the  $3P_{3/2}$  state by dye laser photons. Then sodium ions are produced by collisions in the LEI system, or by photoionization with an N<sub>2</sub> laser in the DLI system, as shown in Figure 26. The pulse durations of dye laser and the N<sub>2</sub> laser are both assumed to be 5 nsec.

The collisional deexcitation rate constant k<sub>21</sub> can
be estimated on the basis of equation (30),

$$\mathbf{k}_{21} = \sum_{a}^{\Sigma} \mathbf{X}_{a} \sigma_{ab} \overline{\mathbf{v}}_{ab}$$
(30)

where  $X_a$  is the particle density of foreign gas a in the flame (159). In our case the burnt gases contain 80% Ar and 20% H<sub>2</sub>0 in the H<sub>2</sub>-0<sub>2</sub>-Ar flame (146).  $\sigma_{ab}$  is the collisional quenching cross section of species b by gas a (here species b indicates sodium), and  $\overline{V}_{ab}$  is the velocity of species a relative to species b, and can be expressed as

$$\overline{v}_{ab} = \sqrt{\frac{8kT}{\mu_{ab}\pi}}$$
(31)

where k is Boltzmann's constant, T is the temperature in K, and  $\mu_{ab}$  is the reduced mass of species a and b. In our case, the flame temperature is  $\sim 2100$  K (146). The collisional excitation rate constant  $k_{21}$  may be obtained directly from  $k_{12}$  using Equation (32),

$$k_{12} = k_{21} \frac{g_2}{g_1} \exp(-\frac{\Delta E_{12}}{kT}),$$
 (32)

where  $\Delta E_{12}$  is the energy difference between the  $3S_{1/2}$  and the  $3P_{3/2}$  state. Similarly, the collisional ionization rate constant  $k_{2i}$  from the  $3P_{3/2}$  state is given by (147)

$$k_{2i} = \sum_{a}^{\Sigma} X_{a} \sigma_{ab}^{*} \overline{V}_{ab} e^{-\Delta E_{2i}/kT}$$
(33)

where  $\sigma_{ab}^{*}$  is the collisional ionization cross section of sodium atoms in the  $3P_{3/2}$  state with the burnt gases in the flame and  $\Delta E_{2i}$  is the energy defect between the  $3P_{3/2}$ state and the continuum. The relationship between  $B_{21}$  and  $A_{21}$  is expressed as (158)

$$A_{21} = \frac{2hv_{21}^3}{C^2} B_{21}$$
(34)

where c is the velocity of light,  $v_{21}$  is the frequency of the transition between the  $3S_{1/2}$  and the  $3P_{3/2}$  states, and h is the Planck's constant.

The photoionization rate constant R from the 3P3/2 state to the continuum can be estimated in terms of the photoionization cross section of sodium by (153),

$$\mathbf{R} = \sigma \phi , \qquad (35)$$

where  $\phi$  is the photon flux in photons/(cm<sup>2</sup>sec). The total energy of one dye photon (at 5890 Å resonant with  $3P_{3/2}$ state) plus one N<sub>2</sub> laser (at 3371 Å) is greater than the ionization energy for sodium by 0.014 Rydberg. The photoionization cross section  $\sigma$  ( $3P_{3/2}$  state to continuum with  $\epsilon$  =0.014 Rydberg) was calculated to be 3.5 x 10<sup>-18</sup> cm<sup>2</sup> by Aymar et al. (145). If we assume a power density of 80 MW/cm<sup>2</sup> for the N<sub>2</sub> laser, the photoionization rate constant is 8.6 x  $10^8 \text{s}^{-1}$ .

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Table. 3 shows the values of the various cross sections, coefficients and rate constants used in the calculations. The relaxation rate constant K is assumed to be in the range of  $10^4$  to  $10^{10}$ s<sup>-1</sup>. Such an assumption is reasonable, because the experimental results for the lifetime of Na<sup>+</sup> are on the order of  $\mu$  sec (146). We shall compare the effects of the relaxation rate constant from the continuum to the  $3P_{3/2}$  state, K(i  $\neq$  2), and from the continuum to the  $3S_{1/2}$  state, K(i  $\neq$  1), on the ion population density in the next section.

#### C. Results and Discussion

Eberly and Daily have come to identical conclusions in examining the validity of the rate equation approach to laser excitation (153,154). Eberly used an equation related to the Rabi frequency and transition rate to examine limitations of the rate equation formulation (153). That is

$$P = \frac{\Omega^2}{\Gamma}$$
(36)

where P is the transition rate under laser excitation,  $\Omega$ is the Rabi frequency and  $\Gamma$  is the absorption line width. Only when P <  $\Omega$  (or  $\Gamma > \Omega$ ), does one have a smooth

1 = 35 <sub>4</sub>		(1) 2	(2) ,	(3) (4) _1 (3)
$2 = 3P_{3/2}$	$^{\prime \pm 6}$ Na - Ar (nm <sup>2</sup> )	$\sigma_{Na} - H_2 O(nm^2)$	<sup>o</sup> Photo. (nm <sup>2</sup> )	$k_{ab}$ (S-1) $A_{21}$ (S <sup>-1</sup> ) $B_{12}$
i = continuum				a, d=1, 2, 1 (Cm Hz/Ws)
1 + 2				$\frac{2.2 \times 10^3}{6.46 \times 10^{17}}$
2 + 1	0.01	0.05		$1.2 \times 10^{8} 6.28 \times 10^{7}$
2 coļl. <sub>i</sub>	27	110		1.4 x 10 <sup>4</sup>
2 phqto. <sub>i</sub>			$3.5 \times 10^{-4}$	8.6 x 10 <sup>8</sup>
i + 2 or 1				$10^4 - 10^{10}$

(1) See reference (160) for quenching cross sections.

 $g_{Na-X}(X = Ar, H_2O; ground continuum) = g_{Na} - X^{(3P_3/2} + continuum);$ the reason was discussed in reference (131) and reference (161). See reference (161) for collisional ionization cross sections;

- (2) See reference (145).
- (3) See text for calculations.
- (4) See reference (162).

monotonic population flow through the atomic levels; i.e. the rate equation formulation is valid under such conditions. Otherwise, population pulsations may occur at the Rabi frequency (155). Similarly, Daily pointed out that the rise time of the laser radiation must be longer than the collisional dephasing time in order to use the rate equation approach. Obviously, the former is related to the Rabi frequency; the latter is related to the absorption line width. We may estimate the Rabi frequency in the flame in comparison with the transition rates to examine the validity of the rate equation approach used in the system. The Rabi frequency of resonant radiation is defined as

$$\Omega = \frac{2dE}{\hbar}$$
(37)

where d is the transition dipole matrix, E is the amplitude of the laser field and  $\pi$  is the Planck's constant divided by  $2\pi$ . The dipole matrix is related to the natural decay rate (spontaneous emission rate) by (163)

$$d_{21} = \left(\frac{3h E}{32 \pi^3}\right)^{\frac{1}{2}} \lambda^{\frac{3}{4}} A_{21} , \qquad (38)$$

where  $\lambda$  is the transition wavelength. The amplitude of the laser field can be expressed as

$$E = \left(\frac{1}{\varepsilon_{0} c} \frac{P_{l}}{A}\right)^{\frac{1}{2}}$$
(39)

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where  $\boldsymbol{\epsilon}_{\bullet}$  is the permittivity of free space, and  $P_{g}$  /A indicates the power density of the laser radiation. Therefore, with a power density of 40 MW/cm<sub>2</sub> (the dye laser power used in the special case B-2),  $\Omega$  is estimated as  $1.6 \times 10^{12} \text{ sec}^{-1}$ . The transition rates used in the system are less than  $10^{10} \text{sec}^{-1}$ , satisfying the inequality P < $\Omega$ Obviously, under the conditions which apply to LEI and DLI, the rate equations employed here are valid.

# C-1 Effects of K on n<sub>i</sub> and n<sub>2</sub>

The relaxation process of a sodium ion depends on several factors such as the recombination rate, the radiative deexcitation rate, diffusion, and mobility. For simplicity, we treat the relaxation process from the continuum as a parameter K. As shown in Figures 27-30, the temporal behavior of fluorescence and ionization with respect to various K values indicates that K has a significant effect on the decay of ionization, which falls faster with increasing K values. A large K value may cause the ion population density to be low in both DLI and LEI, because the ionization probability is offset by a strong deexcitation probability. Also a large K seems to result in a short rise time for the ion population density. On Figure 27. Temporal profiles of ionization in DLI with spectral irradiance of 5 x  $10^{-10}$  W/cm<sup>2</sup> Hz and various K values. A: K =  $10^{6}$  s<sup>-1</sup>; B: K =  $10^{8}$  s<sup>-1</sup>; C: K =  $10^{10}$ s<sup>-1</sup> (From equation (16) to (26) ).



Figure 28. Temporal profiles of ionization in LEI with spectral irradiance of  $5 \times 10^{-10} \text{ W/cm}^2\text{Hz}$  and various K values. A:  $K = 10^6 \text{ s}^{-1}$ ; B:  $K = 10^8 \text{ s}^{-1}$ ; C:  $K = 10^{10} \text{ s}^{-1}$  (From Equations (16) and (26) ).



Figure 29. Temporal profiles of excited state population density (fluorescence) in DLI with spectral irradiance of 5 x  $10^{-10}$  W/cm<sup>2</sup> Hz and various K values. A: K =  $10^{10}$  s<sup>-1</sup>; B: K =  $10^{8}$  s<sup>-1</sup>; C: K =  $10^{6}$  s<sup>-1</sup>.

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Figure 30. Temporal profiles of excited state population density (fluorescence) in LEI with spectral irradiance of 5 x  $10^{-10}$  W/cm<sup>2</sup>HZ; the profiles are identical to each other for K =  $10^{6}$  s<sup>-1</sup>, K =  $10^{8}$  s<sup>-1</sup> and K =  $10^{10}$  s<sup>-1</sup> (from Equation (16) and (26) ).



LEI is independent of the K values, in the range of  $10^4$  to  $10^{10}$ . That is different from the results of DLI, as can be seen by comparing Figure 29 to Figure 30. A larger K may offset the immediate fall of excited state population density in DLI during the period of laser radiation. Such a fast falling tendency is casued by the strong radiative coupling between the excited state and the continuum with the addition of the N<sub>2</sub> laser.

### C-2 Nonsteady State versus Steady State

Figures 31-32 show a comparison of the temporal behavior of the ion population density under steady state conditions  $(dn_2/dt \stackrel{\sim}{} 0)$  and nonsteady state condition for both DLI and LEI. For the larger K values, the ion population density can be treated simply by the steady state case during the laser pulse; i.e. as K increases, the results based on the nonsteady state become approximately the same as those based on the steady state assumption. The K value is related to the lifetime of the ion population; hence after the laser radiation is off,  $n_i$ falls faster with a larger K value.

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Figure 31. Comparison of temporal profiles of ionization in DLI for the nonsteady state case and the steady state case. A:  $K = 10^4 \text{ s}^{-1}$ ; B:  $K = 10^8 \text{ s}^{-1}$ ; and C:  $K = 10^{10} \text{ s}^{-1}$ ; the spectral irradiance is  $10^{-8} \text{ W/cm}^2\text{Hz}$ .

Figure



Figure 32. Comparison of temporal profiles of ionization in LEI for the nonsteady state case and the steady case. A:  $K = 10^4 \text{ s}^{-1}$ ; B:  $K = 10^8 \text{ s}^{-1}$ ; spectral irradiance =  $10^{-8} \text{ W/cm}^{2}\text{Hz}$ .

## C-3 $\underline{n_i}$ and $\underline{n_2}$ with Respect to Spectral Irradiance

Based on Equations (14) and (16), the ion population density is plotted against the spectral irradiance of the dye laser, as shown in Figure 33. The ionization enhancement of DLI with respect to LEI is four orders of magnitude. Here the photoionization rate constant R of DLI was calculated assuming an N<sub>2</sub> laser power density of 80 MW/cm<sup>2</sup>. The deviation of the calculated ionization enhancement from the experimental result of two orders of magnitude may be caused by several factors (131). For example, we have neglected collisional excitation to levels higher than the first excited level of the atom (113). That may increase the ion population in LEI. Also, the power densities of both lasers are not spatially homogeneous in the experiment (148). These factors are apt to cause a high estimate for the enhancement factor. The ion population in DLI is determined mainly by the photoionization rate constant R. shown in Figure 34, the ion population in DLI As is linearly proportional to R, as long as R is at least one order of magnitude larger than the collisional ionization rate constant  $k_{2i}$ . If the N<sub>2</sub> laser power is such that R is less than an order of magnitude greater than  $k_{2i}$ , the nonlinear dependence of the ion signal on the N<sub>2</sub> laser power is expected (see Figure 34). Our previous



Figure 33. Comparison of power dependence of ionization for DLI and LEI. A and C:  $K = 10^4 \text{ s}^{-1}$ ; B and D:  $K = 10^8 \text{ s}^{-1}$ .



Figure 34. The N<sub>2</sub> laser power dependence of ionization in DLI. The N<sub>2</sub> laser power is linearly proportional to the photoionization rate constant R. As R drops below  $10^5 \text{ s}^{-1}$ , ionization  $(\bar{n}_i/n_T)$  as a function of R begins to deviate from the solid line of unity slope, as indicated by the dashed line. The arrow (+) along the R axis denotes the value of the collisional ionization rate constant  $k_{2i}$ . experimental results demonstrated that photoionization dominates the ionization pathway for sodium in DLI, following excitation to the  $3P_{3/2}$  state by a dye laser. Also, the ion signal is proportional to the power density of the N<sub>2</sub> laser ( in Chapter III ). That is in agreement with the calculations shown here.

By contrast, the excited population density  $N_2$  in DLI is on the same order of magnitude as that of LEI, as shown in Figure 35. This calculation agrees with the experimental result; the fluorescence from the  $3P_{3/2}$  to  $3S_{1/2}$  level in the DLI case is not significantly different from that of the LEI case ( in Chapter III). Figure 33 and Figure 35 suggest that it would not be difficult to develope saturation DLI or saturation LEI spectroscopy in flames, comparable with saturated fluorescence spectroscopy, which has been popularly investigated because of the advantage of independence of power density (164-166).

### C-4 Temporal Profiles for Ionization and Fluorescence

The predicted relationship between the temporal behavior of ionization and fluorescence for both DLI and LEI is given in Figures 36-37. Several characteristics of this relationship are as follows: (1) the decay of

Figure 35. Comparison of power dependence of fluorescence for DLI and LEI. A:  $K = 10^4$  or  $10^8 \text{ s}^{-1}$ ; B:  $K \neq 10^8$  $\text{s}^{-1}$ ; C:  $K = 10^4 \text{ s}^{-1}$ . The fluorescence signal is proportional to the excited state population density  $\overline{n}_2/n_{\text{T}}$ .

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Figure 36. The relationship of temporal profiles for ionization, expressed by  $n_i/n_T$ , and fluorescence, expressed by  $n_2/n_T$ , in DLI. A and B are ionization profiles; C and D are fluorescence profiles. A and C: K = 10<sup>8</sup> s<sup>-1</sup>, U = 10<sup>-8</sup> W/cm<sup>2</sup>HZ; B and D: K = 10<sup>8</sup> s<sup>-1</sup>, U = 5 x 10<sup>-10</sup> W/cm<sup>2</sup>HZ.



Figure 37. The relationship of temporal profiles for ionization, expressed by  $n_i/n_T$ , and fluorescence expressed by  $n_2/n_T$ , in LEI. A and B are ionization profiles; C and D are fluorescence profiles. A and C: K = 10<sup>8</sup> s<sup>-1</sup>, U = 10<sup>-8</sup> W/cm<sup>2</sup>Hz; B and D: K = 10<sup>8</sup> s<sup>-1</sup>, U = 5 x 10<sup>-10</sup> W/cm<sup>2</sup>Hz.

fluorescence is much faster than that of ionization; this is also well-known from experiments. The lifetime of fluorescence obtained here is on the order of nsec, in agreement with LIF observations(148). (2) the decay of fluoresence in DLI is faster than that in LEI, because strong radiative coupling links the excited state and continuum in the DLI case. (3) as the spectral irradiance of the dye laser increases, the fluorescence rise time becomes shorter. For example, the fluorescence rise times for both DLI and LEI in Figures 36-37 are less than 0.5 nsec under a spectral irradiance of  $1 \times 10^{-8} \text{ W/cm}^{2}\text{Hz}$ . (4)the strong radiative coupling between the excited state and continuum in DLI leads to the immediate decay of fluorescence even during the period of laser radiation. (5) the ion population density with DLI is four orders of magnitude larger than with LEI; however, the fluorescence (excited state population density) with DLI is on the same order as that of LEI. This shows the same tendency described in the preceeding subsection.

#### C-5 Laser Pulse Duration

As mentioned previously, the aperture duration of the boxcar integrator is set to be the same as the laser pulse duration. Under this condition, the averaged ion

population density for different periods of laser radiation can be obtained by Equation (14). As shown in Figures 38-39, the ion population density of DLI and LEI with  $5 \times 10^{-6}$  sec laser pulse duration is larger than that with a laser pulse duration of  $5 \times 10^{-9}$  sec under the same spectral irradiance. However, the laser pulse duration has a stronger effect on the LEI case. The ionization enhancement ratio, (ratio of the ion population density with a usec pulsed laser to that with a nsec pulsed laser) varies from 10 to  $10^3$  with a variation of the relaxation rate constant K over the range of  $10^8$  s<sup>-1</sup> to  $10^6$  s<sup>-1</sup> (see Figure 39). Obviously, the ionization enhancement obtained by using a longer laser pulse in LEI is a strong function of the relaxation rate constant. By contrast, the K factor does not have such a significant effect on the ionization enhancement obtained with a longer laser pulse in the case of DLI; the value of ionization enhancement is only about two as the ion population approaches steady state. Furthermore, in comparing DLI with a nsec pulsed laser to LEI with a  $\mu$ sec pulsed laser in Figures, 38-39, we find the former yields more ion population density than the latter. This implies that (1) the LEI sensitivity depends strongly on the laser pulse duration, but the DLI sensitivity depends only weakly on the laser pulse duration; (2) the DLI technique may be superior to the LEI technique in detecting trace metal ions in a flame, no matter what laser pulse duration is employed.

Figure 38. Comparison of ionization in DLI induced by a  $\mu$ sec pulsed laser and by a nsec pulsed laser. A: laser pulse duration = 5 x10<sup>-6</sup> sec;

A: laser pulse duration =  $5 \times 10^{-9}$  sec; B: laser pulse duration =  $5 \times 10^{-9}$  sec.



- $\mu$ sec pulsed laser and by a nsec pulsed laser. C: laser pulse duration =  $5 \times 10^{-6} \text{sec}$ ; D: laser pulse duration =  $5 \times 10^{-9}$  sec.
- Comparison of ionization in LEI induced by a
- Figure 39.

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C-6 Continuum to Ground State Coupling

All the calculations presented previously are based on Figure 26 where the continuum and the excited state are assumed to be coupled with a rate constant  $K(i \rightarrow 2)$ and coupling from the continuum to the ground state K(i -> 1) is neglected. Here the reverse case is considered  $K(i \rightarrow 2)$ coupling to the intermediate state is neglected. The ion population density based on coupling to the ground state is compared to that based on coupling to the excited state. Figures 40 and 41 show the results for both DLI and LEI. The ion population density with K (i  $\rightarrow$ > included can be obtained by solving a set of rate 1) equations analogous to Equations (1-4). The result is similar to that based on the process K (i  $\rightarrow$  2), as given in the following:

$$n_1 = D_1 e^{-\lambda_1 t} + D_2 e^{-\lambda_2 t} + \frac{k_{2i}}{\lambda_1 \lambda_2}$$

where

$$\lambda_{1,2} = \frac{1}{2} [(K + B_{12}gU + Z)] = \frac{1}{4}$$

$$\sqrt{(K + B_{12}gU + Z)^2 - 4 [K(B_{12}gU + Z) + B_{12}Uk_{21}]} - (40)}$$

and  $D_1$  and  $D_2$  are analogous to  $C_1$  and  $C_2$  in Equation (21).


Figure 40. The effect of different continuum relaxation processes on the power dependence of ionization in DLI. Dashed line ( --- ) denotes process K(i → 2); solid line denotes process K(i → 1). A: K = 10<sup>6</sup> sec<sup>-1</sup>; B: K = 10<sup>8</sup> sec<sup>-1</sup>.



Figure 41. The effect of different continuum relaxation processes on the power dependence of ionization in LEI. The ionization curves based on both processes  $K(i \rightarrow 1)$  and  $K(i \rightarrow 2)$  are identical. A:  $K = 10^6 \text{ sec}^{-1}$ ; B:  $K = 10^8 \text{ sec}^{-1}$ .

As shown in Figure 41, with LEI identical results are obtained for the average ion population density vs. spectral irradiance for the continuum to ground state coupling and the continuum to excited state coupling. For DLI the deviation between the averaged ion population density for the two coupling schemes is very small, and decreases with increasing spectral irradiance, as shown in Figure 40. Consequently, for a given continuum relaxation rate constant K, whether the lower level is an excited state or the ground state has little influence on the average ion population density for DLI or LEI.

# C-7 <u>Nonsteady State Versus Steady State for Different</u> Laser Pulse Durations

As shown in Figures 42-43, the averaged ion population density for  $\mu$  sec laser pulses is identical under steady state or nonsteady state conditions. However, when nsec laser pulses are used, a difference is apparent, espeically at lower spectral irradiances. Consequently, the steady state formalism may be utilized for prolonged pulse durations; however, with a short pulsed laser, nonsteady state conditions must be considered in the analysis.

Figure 42. Comparison of the power dependence of ionization in DLI nonsteady state case and the steady state case for different laser pulse durations. A: laser pulse duration =  $5 \times 10^{-6}$  sec; B: laser pulse druation =  $5 \times 10^{-9}$  sec. K =  $10^8$  s<sup>-1</sup>.



Figure 43. Comparison of the power dependence of ionization in LEI for the nonsteady state case and the steady state case for different laser pulse durations. C: laser pulse duration =  $5 \times 10^{-6}$ sec; D: laser pulse duration =  $5 \times 10^{-9}$  sec.  $K = 10^8 \text{ s}^{-1}$ .



## D. Conclusion

We have described the relationship between DLI and LEI under various conditions, using a rate equation approach; the applicability of this approach to the flame system has been shown. In this chapter, the numerical results are specific for sodium atoms excited to the  $3P_{3/2}$ state by a dye laser tuned to resonance at 5890 A. In the DLI process excitation is followed by absorption of а photon from the N<sub>2</sub> laser; in the LEI case excitation is followed by collisions with the combustion products in the This special case chosen because most flame. was parameters are available, and the relationship between DLI and LEI has been investigated experimentally. Essentially, the three-level system presented here for DLI and LEI is applicable to any atomic analyte with a specific excited state as the second level provided the appropriate rate constants are used.

We have investigated several aspects of DLI and LEI on the basis of the formulations derived in Section B; these include the temporal behavior of the excited state population (fluorescence) and of the ion population in both DLI and LEI, the validity of the steady state assumption, the effect of the relaxation rate constant K, the enhancement of ionization and fluorescence in DLI as compared to those in LEI, and the impact of the laser

pulse duration. As a result, we have gained insight into the fundamental characteristics of DLI and LEI, and the relationship between the ionization and fluorescence yields in DLI and LEI.

The DLI technique has been shown experimentally to enhance the ionization signal over that obtained with LEI (131). Herein, this enhancement was modeled on the basis of rate equation. Because of its independence of exciting laser spectral irradiance, saturation fluorescence spectroscopy has been widely developed in detecting trace elements. On the basis of the rate equation approach presented here, we expect it would not be difficult to perform a saturation DLI or a saturation LEI spectroscopy with analogous advantages.

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#### CHAPTER V

#### FLAME TEMPERATURE DETERMINATION BY DUAL LASER IONIZATION

## A. Introduction

Current interest in laser-enhanced ionization (LEI) (2-4, 10, 13-15,131) is attributable at least in part to the technique's selectivity and sensitivity to trace elements (10,131). In addition to trace element detection, recent studies have concentrated upon the effects of probe geometry (13) and electrical interference (14-15), and upon the use of dual lasers to enhance ionization (10,131). In this chapter, we report a new application of the dual laser ionization (or DLI) technique: the measurement of flame temperatures.

Typically, measurements of flame temperatures are often carried out by spectroscopic techniques because these methods do not disturb the combustion processes. Especially in high temperature flames, the spectroscopic methods can give accurate results when thermal equilibrium prevails in the flame gases. Among the various conventional spectroscopic methods, the line-reversal (167-170), and two line methods (170-172) have been widely

used. Both methods based on estimates of are the electronic excitation temperature of an atomic species introduced into a flame. The line-reversal method involves comparing the brightness of an emission line from the flame with that of a calibrated continuum background source at the same wavelength (170). The difficulties of this method lie in the background source stability and the reproducibility in flames above 2800 K (170,171). The two-line ratio method is based on the measurement of the relative populations of two different energy levels of a particular atom introduced into the flame. This method is suitable for high temperature flames, plasma-jets and shock-heated gases (170).The two-line ratio method requires reliable transition probabilities or at least the ratio of the transition probabilities of the lines used. Therefore, it is necessary to select carefully those lines which may produce accurate results for the temperature range to be investigated.

Other spectroscopic methods. such as emission-absorption (173), slope (174) and fluorescence (175) are also often used in measuring flame temperatures. In addition, the intensity distribution of the rotational or vibrational lines of a band spectrum has been used to determine flame The principle temperature. of the rotational or vibrational temperature measurements is basically the same as that of the two-line ratio method. Recently, laser-induced fluorescence (LIF) has been

employed to determine electronic flame temperature, temperature and vibrational rotational flame flame temperature (176-178). Winefordner and coworkers reported several methods related to LIF; these are based on linearity between the fluorescence signal and the laser spectral irradiance, and saturation, respectively technique (178 - 179). The conventional spectroscopic normally involves direct line viewing of radiation from a flame which results in the measurement of spatially averaged temperatures. LIF with spatially-resolved excitation and observation processes may provide a method to determine spatially resolved temperature profiles. On the other hand, the employment of the isolated droplet injection technique introduced by Hieftje and Malmstadt (14) can also achieve measurement of spatially resolved temperatures (180). Most spectroscopic methods flame thermodynamic equilibrium, which does assume not necessarily prevail in flames. Daily reported a technique for recovering a true gas translational temperature by analyzing the fluorescence spectrum from the  $2\Sigma^+$  (v' = 0) state of OH (181).

In DLI, one of the two lasers employed is tuned to resonance with a transition of the analyte atom. The flame temperature measurement method presented here is independent of the nature of the resonant transition utilized. Our results, obtained with sodium and lithium as the ionized analytes, illustrate the use of single and àcub tesp with sche by ević is valu 0556 iet ( tech beti effi Det] coe: DTI chai double photon resonant transitions respectively in DLI temperature measurement. The degree of agreement obtained with the different analytes and different excitation schemes, and the agreement with the temperature measured by the line-reversal method in similar flames, provide evidence that the method is accurate. Another indication is the good agreement of our experimental ion mobility values with those determined by others.

As reported previously (131), for some systems DLI offers a two-order of magnitude improvement in trace Na detection over single laser ionization enhancement techniques. An improved understanding of the ion behavior between probe electrodes should aid in optimizing the efficiency of ion collection in both DLI and single laser methods. In addition, the diffusion and mobility coefficients and ion lifetimes determined in the course of DLI flame temperature measurement should prove useful in characterizing ion behavior.

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## B. Experimental

description Α detailed of our experimental apparatus has been presented elsewhere (131). In our implementation of the DLI technique, a tunable dye laser, pumped by an  $N_2$  laser, and a fraction of the beam of the  $N_2$  laser were collinearly aligned and focused on the same, post-combustion region of the  $H_2/0_2/Ar$  flame. Both lasers had a pulse duration of  $\approx$  5 ns; the width of the spectral profile of the dye laser was < 0.1 nm. Atomic sodium (or lithium) was obtained by nebulizing NaCl (or LiCl) solution into the flame with a pneumatic nebulizer.

For sodium, the dye laser (Rhodamine 6G dye) was tuned to the  $3S_{1/2} \rightarrow 3P_{3/2}$  transition (589.0 nm), while for lithium the dye laser (Rhodamine 101 dye) was tuned to the 2S -> 3D two-photon transition (639.2 nm). A pair of voltage-biased nichrome wires (o.7 mm diameter), separated by 5 mm, were suspended inside the flame 10 mm above the burner head. three-dimensional micrometer-driven Α translation stage provided control of the bottom probe position with a precision better than  $\pm$  0.01 mm. The voltage between the biased probes was controlled by a commercial high-voltage power supply with digital readout. The probe current was passed through a load resistor and the resulting voltage drop was the input to a boxcar integrator. A strip-chart recorder and an oscilloscope

were used as output devices. Laser power was measured with a commercial power meter and maintained at constant levels throughout the experiments.

The probe configuration in the apparatus is depicted in Figure 44; the figure also defines the coordinates  $d_t$  and  $d_b$  of the top and bottom probes relative to the laser beams for use in the following theoretical discussion. Because reversal of the bias voltage across the probes demonstrated the superior sensitivity of asymmetric probe configuration when the bottom probe was negative (Figure 45), Na<sup>+</sup> and Li<sup>+</sup> ions were collected at the variously positioned lower probe in all experiments reported here.

The aspect of our DLI experiments that facilitates flame temperature measurement and also distinguishes the technique from CW laser methods is the ease with which ion lifetime  $\xi$  can be measured. The data in Figure 46 are representative of those obtainable with time-resolved DLI experiments. The plot was obtained by triggering the boxcar integrator with the firing of the N<sub>2</sub> laser and temporally scanning the aperture delay, thus acquiring the time profile of the ion signal.



Figure 44. Schematic of probe configuration. The nichrome wire probes A and D were positioned horizontally and parallel to the collinear dye and N<sub>2</sub> laser beams B and C. The laser beams' center was  $\approx$  10 mm above the Mékér-burner head E. The vertical, "displacement from beam center" distance x is defined such that  $d_t > 0 > d_b$ . Figure 45. Asymmetric sensitivity of DLI apparatus to ion signal. Reversal of the probe bias voltage demonstrated the superior sensitivity of the system when cations were collected at the bottom probe. (Ionization signal expressed in arbitrary units.)





Figure 46. Sample strip-chart recorder tracings for the Na<sup>+</sup> ion signal produced by the dual laser apparatus. In case "a" (case "b") the boxcar integrator aperture was 50  $\mu$ s (200  $\mu$ s), d<sub>b</sub> = -0.6 mm(d<sub>b</sub> = -0.1 mm), and the probe voltage was 100 V(0.0 V). The liftime,  $\xi$ , determined in case "a" was 9.2  $\mu$ s and in case "b" was 40.9  $\mu$ s. (Ionization signal expressed in arbitrary units.)

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## C. Theoretical

In previous work (131), we concluded that the predominant trnasport mechanism for ions produced in our DLI apparatus is drift due to the electric field of the probes. By determining ion lifetimes  $\xi$  first as a function of lower probe position  $d_b$  and second as a function of the probes' field, it is possible to determine independent values of the ion diffusion coefficient D and mobility coefficient  $\mu$  with the respective data sets. The flame temperature T can then be calculated with the Einstein relation (182, 183)

$$T = qDk^{-1} \mu^{-1} ,$$
 (1)

where q is the electron charge and k is Boltzmann's constant.

For the single dimension defined by x in Figure 44, the equation of continuity (182) for the ion density n is

$$\partial n(\mathbf{x},t) / \partial t = D_a \partial^2 n(\mathbf{x},t) / \partial x^2$$
 (2)

Substitution of

$$n(x,t) = n_{x}(x) n_{t}(t)$$
 (3)

into Equation (2) followed by equating both sides of the separated result to  $-\xi^{-1}$  yields

$$n_t(t) = \exp(-t/\xi)$$
(4)

and

$$d^{2}n_{x}(x)/dx^{2} + D_{a}^{-1}\xi^{-1}n_{x}(x) = 0$$
 (5)

Under the physically reasonable assumptions that the ions are completely absorbed at the lower probe,

$$n_{\mathbf{x}}(\mathbf{d}_{\mathbf{b}}) = 0 \tag{6}$$

and that the maximum ion population exists in the ionizing laser beam,

$$dn_{x} (0)/dx = 0 (7)$$

Equation (5) leads to the result

$$\xi = 4\pi^{-2} D_a^{-1} d_b^2$$
 (8)

for the lowest mode soulution.

The value of D<sub>a</sub> must be distinguished from the ionic diffusion coefficient D sought for eventual use in Equation (1) because of the ion-accelerating and

electron-slowing space charge effect. Such an effect is expected when the ion density exceeds  $10^7 \text{ cm}^{-3}$  (182); our previous work (131) suggests the existence of a substantially greater ion density in our experiments. Assuming therefore that our DLI flame environment represents the ambipolar diffusion (182) limit with equal electron and ion temperatures, we assert the familiar relation between the apparent and desired coefficients:

$$D_a \approx 2D.$$
 (9)

In the low, homogeneoous field arising from the bias voltage  $\Phi$  between the probes separated by distance L,

$$\mathbf{L} = \mathbf{d}_{t} - \mathbf{d}_{b}, \tag{10}$$

The ionic mobility v can be defined as

$$\mathbf{v} = \boldsymbol{\mu} \boldsymbol{\phi} \mathbf{L}^{-1} \quad , \tag{11}$$

where the mobility coefficient  $\mu$  is to be determined. The ion lifetime  $\xi$  may be interpreted as the time required for an ion formed in the beam (x = 0) to reach the negatively biased probe (x = d<sub>b</sub>),

$$|\mathbf{d}_{\mathbf{b}}| = \mathbf{v}\boldsymbol{\xi} \quad . \tag{12}$$

Hence  $\xi$  and  $\phi$  measurements determine  $\mu$  via

$$\xi = |d_{\rm b}| L_{\mu}^{-1} \phi^{-1} \qquad . \tag{13}$$

Following substitution of the mobility coefficient so obtained and the D value determined by Equation (8) and (9), Equation (1) yields the flame temperature.

## D. Results

In this section we report diffusion coefficients and mobility coefficients for Na<sup>+</sup> and Li<sup>+</sup> in a stoichiometric  $H_2/0_2/Ar$  flame, together with the flame temperature calculated in each of the two cases. A comparison with the work of others and an analysis of the random error in this preliminary implementation of the DLI method are also presented.

In Figure 47, a plot of ion lifetime  $\xi$  versus  $d_b^2$  is given for Li; use of Equations (8) and (9) yields the value  $D^{\text{Li}^+} = 6.7 \pm 0.34 \text{ cm}^2 \text{s}^{-1}$  A linear plot of Na<sup>+</sup> lifetime versus  $d_b^2$  was also obtained, and similar analysis yielded  $D^{\text{Na}^+} = 5.65\pm0.30 \text{ cm}^2 \text{s}^{-1}$ . Reported values for neutral Na are similar but somewhat higher. Ginsel (184,185) reported  $D^{\text{Na}} = 3.2 \text{ cm}^2 \text{s}^{-1}$  for Na in a 2100 K flame and Snelleman (167,185) found  $D^{\text{Na}} = 9.9 \text{ cm}^2 \text{s}^{-1}$  in a



 $C_2H_2/0_2/N_2$  flame at 2440 K. Ashton and Hayhurst (127,129) report D<sup>Na</sup> values between 5.5 and 13 cm<sup>2</sup>s<sup>-1</sup> for several  $H_2/0_2/N_2$  flame compositions. In the case of Li, Ashton and Hayhurst (186) reported D<sup>Li</sup> = 6.8 cm<sup>2</sup>s<sup>-1</sup> at 1920 K and 8.5 cm<sup>2</sup>s<sup>-1</sup> at 2100 K.

With  $|d_{\rm b}| = 0.9$  mm, L = 6.7 mm, and  $10 \le \phi \le 400$  V, Equation (13) and the linear plot of  $\xi$  versus  $\phi^{-1}$  in Figure 48 combine to yield the Na<sup>+</sup> mobility coefficient,  $Na_{\pm} 30.2 \pm 0.6 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  The corresponding value, with  $|d_b|$ = 0.4 mm, L = 4.6 mm for Li<sup>+</sup>, was  $\mu^{\text{Li}^+}$  = 38.6 + 2.1  $cm^2v^{-1}s^{-1}$  Substitution of these mobility coefficients and the diffusion coefficients discussed above into Equation (1) yields two independent estimates of the flame temperature: T = 2171 + 123 K from the Na DLI data and T =2014 + 150 K from the Li DLI data. As shown in Table 4, these temperature values agree fairly well with each other and also with temperatures obtained by other workers (109,110) using different methods ttudy similar flames. The random error estimates reported above were calculated from the standard deviations in the diffusion coefficient,  $S_{p}$ , and in the mobility coefficient,  $S_{u}$ , using the expression

$$S_{T} = qk^{-1}\mu^{-1} (S_{D}^{2} + D^{2}\mu^{-2}S_{\mu}^{2})^{\frac{1}{2}}, \qquad (14)$$

which follows from



Table 4. Acomparison of flame temperatures for similar  $H_2/O_2/Ar$  flames obtained by line reversal and dual laser ionization (DLI) techniques.

Flame	Composition (1	.min <sup>-1</sup> )	T	Method	Reference
<sup>н</sup> 2	0 <sub>2</sub>	Ar	(°K)	Employed	Number
1.00	0.65	3.45	1990	line reversal	110
1.5	0.75	4.5	2000	line reversal	109
1.0	0.5	3.2	2014	Li <sup>+</sup> DLI	this work
1.00	0.50	3.45	2070	line reversal	110
2.0	1.0	4.0	2136	line reversal	109
1.0	0.5	3.2	2171	Na <sup>+</sup> DLI	this work
1.30	0.65	3.45	2210	line reversal	110

$$s_{\rm T}^2 = (\partial T/\partial D)^2 s_{\rm D}^2 + (\partial T/\partial \mu)^2 s_{\mu}^2$$
 (15)

and Equation (1).

DLI values of  $\mu$  and T permit the calculation of reduced mobility coefficients,  $\mu$  , as (182)

$$\mu_0 = (273.16 \text{K/T}) (P_{\text{Ar}} / 760 \text{ Torr}) \mu$$
 (16)

For our 86.5% Ar post-combustion flame,  $P_{Ar}$ % 657 Torr. The reduced mobility coefficient for Na<sup>+</sup> is thus found to be  $\mu_0$ = 3.29 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, which agrees well with Tyndall's drift-tube determination (187),  $\mu_0$  = 3.02 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The reduced mobility coefficient for Li<sup>+</sup> is found to be  $\mu_0$  = 4.53 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> which agrees well with the drift tube determinations (187,188) of  $\mu_0$  = 4.68 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> by Tyndall and  $\mu_0$  =4.56 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> by Takebe et al.

# E. Discussion

A fair assessment of the place of DLI among the many flame temperature measurement techniques (169-172) will require substantial additional investigation. It now appears that the DLI method possesses at least two advantageous features, and we are attempting to effect their development. First, the technique is dependent upon • à V. S đi lir reg upo Thi opti trea attr: theor

the identity of the ionized analyte element only to the extent that the dye laser is tuned to a resonant transition specific to the element used. Thus, special energy level restrictions encountered with the two-line ratio optical method (171,172) are avoided. Second, the wire probes can be suspended anywhere in the flame with very high spatial resolution. Vertical profiles of flame temperature should thus be obtainable; it is possible that the droplet injection technique of Hieftje and Malmstadt (114) may further enhance possible spatial resolution (180). Because the parallel laser beams and electrodes in a horizontal, cylindrical produce and detect ions corridor across the breadth of the flame, a determination of flame temperatures in successive flame annuli is desirable. However, recent evidence (180) of a large, virtually isothermal central zone in a similar flame suggests that the simpler, global estimate of temperature discussed above retains substantial worth.

Several possible sources of error in and limitations of the DLI flame temperature determination require mention. The validity of Equation (9) is dependent upon the existence of ion-electron thermal equilibrium. This assumed equilibrium is similarly required in some optical methods (170,189). In Section C, the theoretica treatment neglects any vertical velocity of the cations attributable to gravity or convection. A more detailed theoretical approach could follow existing treatments
include analogous terms. Figure 45 requires additional investigation and interpretation in the context of convective velocity. The quantitative impact of three experimental design factors must be noted as requiring additional investigation. The finite temporal aperture width of the boxcar integrator can introduce a small error in ξ values. In addition, there is small experimental uncertainty in the location of the collinear laser beams' center; this uncertainty will be reflected in the d<sub>b</sub> values. Extension of the preliminary work reported here will require improved compositional definition and reproducibility of the  $H_2/O_2/Ar$  flame. It is possible that slightly dissimilar flame-gas flow rates degraded the agreement between the Na and Li DLI temperatures.

Recently, Mallard and Smyth (19) reported the use of a single laser in a laser-enhanced ionization ion-mobility study. Besides employing a dual laser apparatus that affords trace atom sensitivity advantages in some cases (131) and obtaining temperatures as well as mobility coefficients, the work reported here differs from that of Mallard and Smyth in that those authors measured laser-pulse to ion-arrival time gap instead of the determining  $\xi$ . As discussed above, measurements permit the easy estimation of both D and,  $\mu$ , but competitive ion-depletion processes may introduce additional signal decay time constants of the same magnitude as  $\xi$ , a problem now under investigation (192). It is interesting to note

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the excellent agreement of our measured value  $(\mu_{Li} + / \mu_{Na} +) =$ 1.28, with the experimental mobility ratios obtained by Mallard and Smyth (19) in C<sub>2</sub>H<sub>2</sub>/air and CO/O<sub>2</sub> flames.

In summary, it appears fair to characterize dual-laser ionization as a potentially attractive method for the determination of flame temperatures, diffusion coefficients, and mobility coefficients as well as ion lifetimes. Such capabilities strengthen the case for the continued application and development of DLI techniques.

#### CHAPTER VI

# ALTERNATIVE APPROXIMATIONS BASED ON THE EQUATION OF CONTINUITY

# A. Introduction

The dual laser ionization (DLI) technique in flames has been discussed in previous chapters. The design of probe detectors used in DLI is simple, but the elucidation of ion behavior is not easy. The development of probe theories, since the 1920's, has provided the fundamental basis for charged particle behavior in a plasma or a plasma-like system (5). From the basic current-voltage curves of plasmas in which the probes are embedded, the fundamental characteristics of the plasmas, such as electron temperature, electron density and the potential distribution, can be determined. However, most theories assume collisionless conditions or permit only a few collisions; the valid domains of some of these theoretical models have been examined by Waymouth (193), and are described by the ratio of the probe dimensions and the

mean free path of charged particles to the Debye length (193). Schulz and Brown have attempted to extend such models to the case of collision-dominated systems (194). A review of the theoretical and experimental developments in electric probes has been given by Chen (195).

A model is presented to describe the saturation ion current in this chapter. In addition, the ion density induced by DLI in the flame can be approximately estimated with this model.

# B. Theoretical Basis

The sheath dimension usually serves as a useful parameter with which to characterize probe behavior. The determination of probe sheath thickness has been investigated. A theoretical formulation yielding the sheath-thickness under collisionless conditions was first presented by Langmuir (196). That is,

$$\lambda_{s} = \frac{2}{3} \left(\frac{\xi_{o}}{j_{i}}\right)^{\frac{1}{2}} \left(\frac{2e}{M}\right)^{\frac{1}{4}} \phi_{p}^{3/4}$$
(1)

under the assumption that the electric field E and potential V are equal to zero at the sheath edge (196). The symbols used in Equation (1) are  $\lambda_s$ , sheath thickness;  $\epsilon_s$ , , permittivity of free space;  $j_i$ , current density; e, electron charge; M, analyte mass; and  $\phi_p$ , biasing voltage. The collisionless conditions of Equation (1) are inconsistent with those of our atmospheric flame system.

From an approximation theory viewpoint, Biblarz et al. considered the sheath thickness in a collision – dominated MHD plasma (197). From Poisson's equation, a relation between sheath thickness  $\lambda_s$  and Debye length  $\lambda_D$  can be approximately estimated as follows(197):

$$\lambda_{s} = \lambda_{D} \left(\frac{e\phi_{p}}{kT_{e}}\right)^{\frac{1}{2}}$$
(2)

$$\lambda_{\rm D} = \left(\frac{\epsilon_{\rm o} k T_{\rm e}}{n_{\rm o} e^2}\right)^{\frac{1}{2}} , \qquad (3)$$

where  $\phi_p$  is the probe bias-voltage; k is the Boltzmann constant;  $T_e$  is electron temperature; and  $n_o$  is the initial ion density. In relation to Equation (1), Equation (2) is more reliable for estimates of sheath thickness around the wire probe in a flame, because collision-dominated conditions for both MHD plasmas and flames are similar. In the flame, thermodynamic equilibrium,  $T_e = T_i$ , is assumed.

For Langmuir probe theory in collisionless environments it is assumed that no electric field can penetrate through the sheath edge, and both ions and electrons have a Maxwellian velocity distribution at the sheath edge (159). Therefore, the random ion current density  $J_r$  reaching the sheath edge is given as follows:

$$J_{r} = e n_{0} \left(\frac{kT_{i}}{2\pi M}\right)^{\frac{1}{2}}$$
 (4)

The velocity factor  $\left(\frac{kT_i}{2\pi M}\right)^{\frac{1}{2}}$  results from the assumption of the Maxwellian velocity distribution. Bohm improved this model by applying the physically has reasonable condition that the sheath cannot completely shield the electric probe. As a result, the electric field may "leak" out from the sheath to some extent, and accelerate the charged particles arriving at the sheath edge (198). However, this model is only applicable to the collisionless, high density plasma (198,199). Waymouth assumed a diffusion-controlled gas discharge in the quasi-neutral region up to the sheath edge (193). He asserted the domain of his model to be  $\frac{\lambda_c}{r_p} < 10$ ,  $r_p/100 \lambda_p > 1$  and  $\lambda_c/\lambda_p > 10$ , where  $r_p$  is the probe radius and  $\lambda_c$  is the particle mean free path.

By contrast, the case of the sodium ion induced by DLI is collisionally dominated before reaching the probe. Several assumptions are made before deriving a simple model to describe the ion motion to the electrostatic probe. They are:

(1) The sheath along the probe is so thin that the ions may be collected completely by the bottom probe as they reach the sheath edge. The estimation of sheath thickness in the next section indicates the assumption is physically resonable. Thus we may avoid treating the orbital motion of the ions under this assumption (195).

(2) AS the probe is biased, the mobility-controlled motion of the sodium ion controls the ion velocity in the quasi-neutral region, instead of the thermal velocity or diffusion-controlled discharge presented by Langmuir and Waymouth, respectively, in a collisionless gas discharge (5,193). This assumption is based on the experimental evidence, as presented in Chapter V. In addition, Brown reached the conclusion in his model same under many-collision conditions, by using microwaves to measure independently the ion density in the gas discharge (194).

(3) As the Langmuir probe is biased strongly negative, only ions reach this probe; i.e. for saturation ion current collection, the electrons can be repelled completely from the negative probe. This condition is required for elucidation of the steady-state current voltage characteristics (195).

(4) The equation of continuity can be applied approximately to interpret the spatial and temporal behavior of ions in the collision-dominated atmospheric flame (182,200).

In a simple model, the mobility-controlled motion of ions extends up to the sheath edge, as illustrated in Figure 49. The saturation ion current, I<sub>is</sub>, reaching the sheath edge can be expressed as

$$I_{is} = j_{is} A_{s}$$
(5)



Figure 49. Model of ionized particles disturbed by a negative biased probe. The quasi-neutral region is extended up to the sheath edge. The ion velocity is controlled by mobility in this region.  $\lambda_s$  is the sheath thickness; r p is the probe radius.

$$= 1/2 \operatorname{en}_{i} V_{i} A_{s} , \qquad (6)$$

where the constant 1/2 arises from assuming that the sheath thickness is smaller than the probe dimensions, as discussed in detail by Chen (195);  $n_i$  indicates the ion density reaching the sheath edge;  $V_i$  is the average ion velocity dominated by ion mobility;  $A_s$  is the surface area of the sheath (approximately equal to the probe area ) and  $j_{is}$  is the saturation ion current density. Since only the ion current can be collected (given sufficient negative bias on the Langmuir probe), Equation (6) neglects any contribution from electron current.

The mobility-controlled velocity is defined as

$$\mathbf{V}_{i} = \boldsymbol{\mu}_{i} \mathbf{E}$$
 (7)

where  $\mu_i$  is the ionic mobility coefficient and E is the electric field. Under the quasi-neutral condition, that is,  $n_e \approx n_i$ , the electric field E can be considered as constant. The Poisson equation

$$\nabla^2 \phi = -4\pi e(n_i - n_e)$$
(8)  
= 0

implies

$$\nabla \phi = -E = \text{const.} \tag{9}$$

Applying the boundary conditions and integrating Equation

(9) yields

$$E = -\frac{\phi_p}{L}$$
(10)

where  $\phi_p$  is the probe bias-voltage, and L is the interprobe distance.

As in Chapter V, the equation of continuity is used to describe the ion density. Under the assumptions made previously, the diffusive motion of ions outside the sheath edge can be neglected. Therefore one obtains

$$\frac{\partial^{2} n_{i}}{\partial t^{2}} = D_{a} \nabla^{2} n_{i} - \mu_{i} \nabla \cdot n_{i} E \qquad (11)$$

$$\frac{\partial^{2} n_{i}}{\partial t^{2}} - -\mu_{i} \nabla \cdot n_{i} E \qquad (12)$$

Substitution of  $n_i(x,t) = n_x(x)n_t(t)$  into Equation (12) leads to

$$n_t(t) = \exp(-t/\xi)$$
 (13)

and

$$\nabla \cdot \mathbf{n}_{\mathbf{x}} \mathbf{E} - \frac{\mathbf{n}_{\mathbf{x}}}{\mu_{\mathbf{i}}\xi} = 0 \qquad (14)$$

where  $\xi$  is the lifetime.

Substitution of the lifetime obtained in Chapter V,

$$\xi = \frac{|\mathbf{d}_{\mathbf{b}}|\mathbf{L}}{\mu_{\mathbf{i}}\Phi_{\mathbf{p}}}$$
(15)

into Equation (14) yields

$$n_{x}(x) = n_{o} \exp\left(-\frac{x}{d_{b}}\right)$$
(16)

where n, is the initial ion density produced in the ionizing beam, and  $d_b$  is the distance from the ionizing beam to the bottom probe. Therefore, from Equations (13) and (16), the ion density can be expressed as

$$n_{i}(x,t) = n_{o} \exp(-\frac{x}{d_{b}}) \exp(-t/\xi)$$
 (17)

Inserting Equations (7), (10) and (17) into Equations (6) leads to

$$I_{is} = \frac{1}{2} e n_{o} exp(-\frac{x}{d_{b}}) exp(-\frac{t}{\xi}) \mu_{i} A_{s} \frac{\phi_{p}}{L}$$

$$\approx \frac{1}{2} e n_{o} exp(-\frac{x}{d_{b}}) exp(-\frac{t}{\xi}) \mu_{i} A_{p} \frac{\phi_{p}}{L}$$
(18)

where  $A_s \simeq A_p$ . Here  $n_i$  is defined as the ion density reaching the sheath edge; the ions need take  $t \simeq \xi$  to arrive at the sheath,  $x \simeq d_b$ . Thus the saturation ion current  $I_{is}$  can be simplified as

$$I_{is} = \frac{1}{2} e_{n_{o}} exp(-2) \mu_{i} A \frac{\Phi_{p}}{p L} . \qquad (19)$$

In contrast, while the sheath is considered thick enough to allow numerous collisions in it, the ion density of Poisson's equation can be replaced by Equation (6). Electron density  $n_e$  is neglected in the sheath. Under the assumption that the electric field and potential equal zero at the sheath edge (194,195),

$$I_{is} = 2\pi \mu_{i} \epsilon_{o} \ell \phi_{p}^{2} r_{p}^{-2} \gamma^{-2}$$
(20)

where

$$\gamma = \left[ \left( \frac{\lambda_{s}}{r_{p}} \right)^{2} - 1 \right]^{\frac{1}{2}} - \left( \frac{\lambda_{s}}{r_{p}} \right) \ln \left\{ \frac{\lambda_{s}}{r_{p}} + \left[ \left( \frac{\lambda_{s}^{2}}{r_{p}^{2}} \right) - 1 \right]^{\frac{1}{2}} \right\}$$
(21)

and  $\ell$  is the collecting length of the cylindrical probe, r<sub>p</sub> is the probe radius and  $\lambda_s$  is the sheath dimension.

#### C. Results and Discussion

The steady state current-voltage curve can be divided into three regions: the positive ion saturation region, the transition (or partial collection of electrons region) and the electron saturation region (195). We have obtained analogous current-voltage curves previously (146). As the Langmuir probe is biased stongly negative, all the electrons are repelled and this probe collects only the positive ions. That is called ion saturation. As the biasing voltage is diminished, the negative probe begins to collect electrons due to thermal velocity; thus the ion current, compensated by partial electron current, decreases with decreasing negative biasing voltage applied to the Langmuir probe.

As shown in Figure 50, for ion current vs. negative voltage, the net ion current becomes smaller as the probe-beam distance d<sub>b</sub> increases. The distance d<sub>b</sub> changes from 3 mm to 1.5 mm; the ion current in the region of the about transition changes by 180%. Obviously, by considering the probe position the optimum DLI sensitivity in a flame is obtained by placing the negative biased probe as close to the ionizing eam as possible. This may reflect the increased probability of ion neutralization by collisions with foreign gases in the flame as the ion to probe path is increased. Most of the gases have a mean free path of the order of  $10^{-8}$  m under atmospheric conditions (201). Consequently, even a 1 mm variation of beam to path distance may give rise to numerous collisions between ions and foreign gases.

The applicable domain of Equation (19) is for the saturation ion current under strongly negative bias voltage on the Langmuir probe. We select values of 100 volts and 300 volts, respectively, which are located in the region of the plateau ( saturated ion current ), and we plot ion current against the reciprocal probe distance in Figure 51 and Figure 52. A straight line is obtained. Based on Equation (6), the ion density  $n_o$  can be estimated to be  $10^{10}$  cm<sup>-3</sup> from the slope of Figure 51, using the known values of the parameters,  $A_p \sim 1 \text{ cm}^2$ ,  $\phi_p = 100 \text{ volt}$ ,  $\mu_i = 30 \text{ cm}^2/(\text{volt sec})$  (146) and peak amplitude of ion signal = 40 mv on the oscilloscope ( for a load







Figure 51. A plot of ion signal vs. the reciprocal of interprobe distance. Sodium ion is induced by DLI  $(3S_1 \rightarrow 3P_{3/2})$ , Biasing voltage on the bottom probe = -100 volt. The distance between top probe and ionizing beam is fixed at 4.25 mm. The arrow along Y axis indicates the amplitude of 40 mv observed on the oscilloscope.



Figure 52. A plot of ionization vs. the reciprocal of interprobe distance. Sodium ion is produced by DLI( $3S_1 \rightarrow 3P_3/2$ ). Biasing voltage = -300 volt. The distance between the top probe and the ionizing beam is fixed at 4.25 mm.

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resistor,  $R_1 = 50 \ K_{\Omega}$ ,  $I_{is} \sim 8 \ x \ 10^{-7}$  amp). This estimate is reasonable in comparison with the previous value for the ion number generated during a laser pulse (131). Applying the values of  $n_0 = 10^{10} \ cm^{-3}$ ,  $\phi_p = 100$  volt and  $T_i \simeq T_e \simeq 2100$ K (obtained previously) in Equations (2) and (3) leads to  $\lambda_D \simeq 2 \ x \ 10^{-2} \ mm \ and \lambda_s \simeq 6 \ x \ 10^{-1} \ mm$ . The sheath thickness has been assumed to be smaller than the probe diameter which is  $\sim 1 \ mm$ . This result is consistent with the assumption.

By contrast, if bias voltages of 20 volts and 30 volts are selected from the transition region of the probe characteristic curve in Figure 50, a nonlinear plot of ion current against reciprocal probe distance is obtained, as shown in Figure 53 and 54, respectively. The ion current is partially balanced by absorption of electrons at the probe in the transition region, as follows:

$$I = 1/2 A_{s} \sum_{j} V_{j}^{n}_{j}_{j}$$

$$= 1/2 A_{s} V_{i}^{n}_{i} - 1/2 A_{s}^{n}_{e}^{n}_{e}$$
(22)

That is the reason why Equation (19) cannot be applied to the transition region.

From the Equation (20), the saturation ion current is expected to be proportional to the square of biasing voltage; however, as shown in Figure 50, the ion current in the saturation region decreases to some extent as the biasing voltage becomes larger. The failure of Equation



Figure 53. A plot of ionization vs. reciprocal of interprobe distance. Sodium ion is produced by DLI( $3S_1 \rightarrow 3P_{3/2}$ ). Biasing voltage = -20 volt. The distance between the top probe and the ionizing beam is fixed at 4.25 mm.



Figure 54. A plot of ionization vs. reciprocal of interprobe distance. Sodium ion is produced by DLI  $(3S_{k} \rightarrow 3P_{3/2})$ . Biasing voltage = -30 volt. The distance between the top probe and the ionizing beam is fixed at 4.25 mm.

(20) to fit the experimental results is caused by the assumptions of this model. (1) The electric voltage is treated as zero at the sheath edge; actually, some electric field may penetrate the sheath (198). (2) The condition is for sheath thickness >> probe dimension, not like the thin sheath we have in the system. Chen pointed out that such a condition is unusual unless a magnetic field is applied (195).

As the biased voltage of the bottom probe becomes less negative, more electrons are absorbed and the ion current becomes smaller. As the bias voltage changes towards positive values, more electrons are collected to balance the ion current. The point where no net current can be detected is called the floating voltage. As shown in Figure 55, a relation between beam-probe distance  $d_b$ and applied positive voltage indicates the floating voltage decreases as  $d_b$  increases, due to the electron velocity being much larger than the ion velocity. Less positive voltage is needed to maintain the net current equal to zero.

## D. Conclusion

Based on several physically resonable assumptions, a formalism has been used to characterize the behavior of



Figure 55. Floating potential vs. distance from bottom probe to ionizing beam. The distance between the top probe and the ionizing beam is fixed at 5.0 mm.

the saturated ion current. In addition, the ion density may be estimated with this formalism. Ion signal sensitivity to biasing voltage and the reciprocal of the interprobe distance has been shown.

In fact, we must recognize some limitations in the model described in Section B, such as : (1) the reference probe is too small to fit the assumption used in the Langmuir probe theory (195); (2) any emission of electrons by the probe in the flame, which may disturb the ion current, is neglected; (3) the effect of sheath thickness on the potential distribution is neglected; and (4) the boundary conditions cannot fit Equation (16), which may reflect the neglect of difusion in treating the equation of continuity (131). Possible improvements, such as increasing the area of the reference probe, and insulating the portion of the probe outside the flame may eliminate some of the difficulties.

#### CHAPTER VII

# THE EFFICACY OF DLI IN AN H2-02-Ar FLAME

#### A.Introduction

Recently, research in laser-induced ionization has become a very important area of spectroscopy. This technique differs from a normal optical spectroscopic technique in at least two characteristics: (1) the former involves the ionization continuum of the analytes, whereas the latter deals with the discrete states; (2) an ion detector is employed in the former, whereas an optical detector is used in the latter.

The advantages of an ion detector over an optical detector include freedom from light scattering, no solid angle restrictions and higher efficiency. Basically, an atom can be converted into a positive ion and an electron with the aid of a laser; therefore the detection efficiency can be rearly unity, whereas the quantum efficiency of photomultiplier tubes is < 0.50 (22). Ion detectors employed in a laser-induced ionization technique include thermionic diodes, proportional counters, ionization chambers, electron multipliers, mass spectrometers and electrostatic probes. Laser-induced

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ionization techniques can be classified according to the detection system used, the sample type, the atomization system and the ionization process. Thus, there are methods such as resonance ionization spectroscopy (RIS) (22), multiphoton ionization spectroscopy (MPI) (86) and laser-enhanced ionization (LEI) (2).

application of the optogalvanic effect in An flames, called LEI was introduced in 1976 (2,3). LEI is a technique to detect analytes introduced in a flame with a laser tuned to resonance with a particular energy level. Collisional ionization becomes more efficient for analytes starting from an excited state than from the ground states. The collisional ionization rate constant is enhanced by decreasing the energy defect between the ionization continuum and the discrete excited state, on the basis of the Boltzmann distribution (147).Current research in LEI, primarily carried out by scientists at the National Bureau of Standards (NBS), includes trace metal analysis (6-8), electrical interference studies (14,15), and molecular LEI (16-18). In trace metal analysis, various methods related to laser design and detection systems have been attempted to improve the sensitivity and selectivity of ion detection; detection limits as low as 0.001 parts per billion (ppb) can be achieved for some elements (2).

Dual laser ionization (DLI) is similar to LEI, but employs two lasers in producing the analyte ions in flames

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(131,146). In DLI, an N<sub>2</sub> laser-pumped dye laser is tuned to a resonance transition of an analyte; ions are produced by the N<sub>2</sub> pumping laser which has sufficient photon energy to cause photoionization (131,146). The energy level scheme used in DLI differs from that used in stepwise LEI with two dye lasers; in the latter each dye laser is resonant with a particular excited state, and the two lasers share a common intermediate state. This difference may result in a different ionization process following the dye laser excitation. Multiphoton ionization is predominant in DLI as the dye laser is tuned to the transition of the  $3S_{1/2}$  to  $3P_{3/2}$  level of sodium (Chapter III), whereas the collisional ionization process is favored with decreasing the energy defect between the continuum and the discrete state by stepwise excitation (6).

If we consider the analyte in DLI to be a three-level atomic system, ion production can be related to the collisional ionization rate constant and the photoionization rate constant for the analyte in its populating the excited state, as treated by the rate equation approach in Chapter IV. Which of these processes dominates depends on the magnitude of these two factors. In this chapter, various ionization schemes of sodium and lithium are examined in order to extend the applicability of competition DLI. In addition, the between photoionization and collisional ionization is tested

experimentally and the results are compared with predictions based on the rate equation approach and other theoretical models. Finally, the detection sensitivity of DLI is compared with that of LEI.

#### B. Experimental

The two DLI beams are obtained by directing an  $N_2$  laser-pumped dye laser and a portion of the  $N_2$  pump laser into the same area of an  $H_2$ - $O_2$ -Ar flame. The beams are directed collinearly from opposite directions, with maximum temporal and spatial overlap over the burner head. The pulse durations of the two lasers are 5nsec. This is an inexpensive way to gain a dual-beam construction. An analogous design has also been used elsewhere (202).

A premixed  $H_2-O_2$ -Ar flame was used, with a temperature about 2100 K as determined by the DLI method of Chapter V. Free atoms of the alkali selected element were obtained in the flame by driving the corresponding alkali chloride solution out of a pneumatic nebulizer with Ar gas. The dye laser was tuned to resonance with transitions to a higher energy level of the atom from either the ground or thermally excited states to produce the population in the upper states via one- or two-photon absorption; the ions produced were then collected by a

pair of voltage-biased nichrome wires suspended parallel to one another inside the flame. The resulting ion current passed through an electronic network where it was converted to the voltage domain; this voltage signal was the input to a boxcar integrator for signal processing. The readout system was a strip chart recorder and an oscilloscope. Several organic dyes were employed in the experiment for selection of various excitation wavelength ranges. Rhodamine 6G was used for  $3S \rightarrow 3P$  one-photon and the  $3S \rightarrow 4D$  two-photon transitions of sodium; Rhodamine B was used for the  $3S \rightarrow 5S$  two-photon and the  $3P \rightarrow 5S$  one-photon transitions of sodium; DCM was used for the  $2S \rightarrow 2P$ one-photon transition of lithium, and Rhodamine 101 was used for the 2S - 3D two-photon transition of lithium. A photomultiplier tube in connection with a monochromator was employed to monitor the selected dye laser wavelength.

The output power of the dye laser was varied by inserting neutral density filters between the flame and the front mirror of the laser cavity. The set of neutral density filters, recalibrated at 3371 Å with a UV/VIS spectrophotometer (Cary 17), was also used to vary the output power of the N<sub>2</sub> laser.

Solutions containing 100  $\mu$ g/ml (ppm) Na (NaCl) and 100  $\mu$ g/ml Li (LiCl) were used throughout the experiments, except for the case of the 3P  $\rightarrow$  5S transition of Na and the 2S  $\rightarrow$  3D two-photon transition of Li, where solutions containing 1000  $\mu$ g/ml were used.

## C. Results and Discussion

In order to study the effect of the  $N_2$  laser on ionization enhancement in DLI and on the ionization pathways, the energy level schemes of Na and Li shown in Figure 56 were employed. In all cases except for the scheme shown in Figure 56d, the dye laser is tuned to a one- or two-photon transition of the analyte from the ground state and the  $N_2$  laser or collisions produce ionization. In the case of the scheme in figure 56d, the dye laser promotes the analyte to the 5S level from the thermally-produced excited 3P level.

# C-1 Ion Background

-The ion signal induced by DLI is more complex than that in LEI. LEI signals can be observed by blocking the  $N_2$  laser beam. A significantly large ion background was observed in DLI with respect to LEI as exemplified by the Li (2S-3D) two-photon resonance in Figure 57. Therefore, careful selection of the proper baseline under each set of experimental conditions is necessary for power dependence Figure 56. Energy schemes for sodium and lithium DLI. A dye laser is tuned to a transition to an excited state via one- or two-photon absorption from the ground state or a thermally excited state; the wavelength in Å is specified. The second  $(N_2: \lambda = 3371 \text{ Å})$  laser provides energy sufficient to reach the ionization continuum.



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Ion signals obtained when the dye laser is tuned through the two-photon  $(2S \div 3D)$  excitation of Li: Figure 56 (f). (a) DLI, (b) LEI. Figure 57.

studies. Sources for the ion background in DLI include: (1) the dye laser; (2) the  $N_2$  laser; (3) the flame; (4) the broadband lasing of the organic dye. This latter probably occurs between one wall of the dye cuvette and the end mirror. Broadband lasing occurs over a range of wavelengths and depends on the dye employed. Thermal ionization from the flame is, however, constant with time and not detected by the gated integrator. For example, the laser output and the broadband lasing from Rhodamine B are shown in Figure 58. Because of the presence of two lasers and broadband lasing, there are several baselines induced by DLI, as shown in Figure 59. For convenience, the notation I (P1, P2, F, T) is used to indicate the ion background signal as a function of the  $N_2$  laser power  $P_1$ , the dye laser power  $P_2$ , the broadband lasing F and the flame temperature T. Therefore, signal I<sub>1</sub>(P<sub>1</sub>, P<sub>2</sub>, F, T,) is obtained with irradiation by both the dye laser and the  $N_2$  laser; signal  $I_2(P_1, F, T)$  is obtained when the dye laser is blocked;  $I_3(P_1, T)$  is obtained under  $N_2$  laser irradiation alone;  $I_{\underline{A}}(T)$  is obtained by blocking both lasers. Obviously,  $I_2(P_1, F,T)$  is selected as the baseline for DLi and  $I_1 - I_2$  is plotted against dye laser power for the measurement of dye laser power dependence. Similarly,  $I_2 - I_3$  is selected for the measurement of power dependence of broadband lasing. When the signal  $I_3(P_1, T)$ -  $I_{A}(T)$  is plotted against the N<sub>2</sub> laser power, a slope of one is obtained. This demonstrates that this background Figure 58. Lasing at 6154 Å plus broadband emission (over  $\sim$  100 Å rang) produced by a Rhodamine B tunable dye laser.




Figure 59. Ion signals obtained for the energy scheme of Figure 56 (c)  $[Na(3S \rightarrow 5S) \text{ two-photon excitation}]$ under various experimental conditions.  $I_1$  $(P_1, P_2, F, T)$  denotes ionization due to the  $N_2$  laser  $P_1$ , dye laser  $P_2$ , broadband lasing F and flame temperature T; similar definitions apply to  $I_2(P_1, F, T)$ ,  $I_3(P_1, T)$  and  $I_4(T)$ . contribution comes from the thermal population of sodium (3P level) followed by absorption of one photon from the N<sub>2</sub> laser. This thermally-based ionization process is analogous to the resonance case of Figure 56a. The background contributed by  $I_3 - I_4$  depends on the alkali concentration, and it seems to be negligible when less than 100 µg/ml Na concentration is used. Based on the Boltzmann distribution, the thermal population ratio of 4S level to the 3P level is 2.5 x  $10^{-3}$ ; thus the ionization emanating from other thermally-populated excited states can be ignored. Multiphoton ionization by absorption of two photons from the  $N_2$  laser has not been observed for Na. Frank Curran (203) has, however, observed off-resonant multiphoton ionization for Cs, and K.

The background  $I_2 - I_3$  induced by broadband lasing is linearly proportional to the power of the  $N_2$  laser and to the power of the broadband emission. Figure 60 shows the dependence of the ion background  $I_2 - I_3$  on the power of the broadband emission. Accordingly, the  $N_2$  laser in DLI can increase the backgound ionization by photoionization of excited levels produced thermally or by absorption of broadband radiation.



Figure 60. Relative ionization from Na as a function of the power of broadband lasing from Rhodamine 6G, at constant N<sub>2</sub> laser power. The log-log plot gives a straight line with slope = 1.

# C-2 <u>Sodium Ionization with 3S - 4D Two-photon Resonance</u> Excitation

Sodium DLI with 3S - 3P resonance excitation (Figure 56a) is discussed in Chapter III and Appendix A. The experimental ionization enhancement of DLI over LEI in magnitude, orders of that case is about two and photoionization is the predominant process following the (one-photon) dye laser excitation. As shown in Figure 61, sodium DLI and LEI, respectively, in the case of 3S - 4D two-photon absorption (Figure 56b), properly depends on the square of the dye laser power. Moreover, here the presence of the second (N2) laser in DLI provides no significant ionization enhancement. Clearly, this result demonstrates that collisional ionization must dominate both DLI and LEI, following the two-photon excitation by the dye laser. The predominance of collisional ionization over photoionization results in there being little effect of adding the N<sub>2</sub> laser in DLI. Thus, ionization under the conditions shown in Figure 56b follows a different pathway and shows different sensitivity, compared to the case depicted in Figure 56a.

In order to estimate the contribution of multiphoton ionization to DLI with 3S - 4D two-photon absorption, we assume both DLI and LEI undergo the process



of multiphoton ionization, as follows,

$$Na(3S_{1/2}) + 2hv(5787 Å) + Na(4D_{3/2}) + hv + Na^{+} + e$$
  
 $Na(3S_{1/2}) + 2hv(5787 Å) + Na(4D_{3/2}) + hv +$   
 $hv'(3371 Å) + Na^{+} + e$ 

Ionization rates were calcualted from Equation (1), which is based on an analogous equation in ref(124):

$$W = \sum_{j=1}^{2} |B_{2j}|^{2} \left( E_{1f}^{2} |z_{k2}|^{2} + E_{2f}^{2} |z_{k'2}|^{2} \right)$$
(1)

Here W denotes the overall ionization rate for DLI, and the first term of Equation (1) indicates the ionization rate for LEI;  ${}^{2}_{L}\beta_{2j}|^{2}$  indicates the two-photon transition probability from the 3S to the 4D state;  $E_{1}$  and  $E_{2}$  are the field amplitude of the dye laser and the  $N_{2}$  laser, respectively;  $Z_{k2}$  and  $Z_{k'2}$  are dipole matrix elements connecting the  $4D_{3/2}$  level and the level of the continuum appropriate for the dye laser and the  $N_{2}$  laser, respectively. The ratio of the calculated multiphoton ionization rates for DLI over LEI is 1.1 when the power density is taken as 70 MW/cm<sup>2</sup> for the dye laser and 80 MW/cm<sup>2</sup> for the  $N_{2}$  laser. This calculation reveals that, unlike the case treated earlier (3S - 3P), under 3S - 4D resonance excitation there is no significant enhancement by adding an  $N_{2}$  laser photon over photoionization with three dye laser photons. The calculated results differ for these two cases because two dye laser photons are required in LEI (figure 56a) for photoionization from the 3P level, whereas only a single dye laser photon is required in LEI, from the 4D level (Figure 56b). It is well-known that a two-photon ionization cross section for an excited state atom will be much smaller than that for single-photon ionization (77).

According to the three-level rate equation treatment given in Chapter IV, the competition between photoionization and collisional ionization following dye laser excitation depends primarily on the values of the constant and collisional photoionization rate the ionization rate constant for the intermediate, excited state of the analyte. In order for photoionization to dominate, the photoionization rate constant must be larger than the collisional ionization rate constant by at least one order of magnitude (Chapter IV). Under this condition, the collisional ionization process is negligible. Based on the Boltzmann distribution, the collisional ionization rate can be enhanced nearly exponentially by decreasing the energy defect between the continuum and the excited state. The collisional ionization rate constant can be estimated from Equation (2) : (147)

$$K = \sum_{j} [X_{j}] \sigma_{M^{\star}, x_{j}} \left(\frac{8\pi kT}{\mu_{M, x_{j}}}\right)^{\frac{1}{2}} \exp\left(-E/kT\right)$$
(2)

Here K is the ionization rate constant; [x,] is the concentration of component  $x_i$  in the  $H_2-O_2$ -Ar flame (in our case the flame gases after combustion contain about 80% Ar as the major colliwion partner with alkali atoms, and about 20%  $H_2O$ ).  $\sigma_{M^*,x_i}$  indicates the ionization cross section between an excited alkali atom  $M^*$  and  $x_{j}$ ;  $\mu_{M,X_{i}}$  is the reduced mass of M and  $x_{i}$ ; E is the energy defect between the excited state and the continuum. In comparing collisional ionization rate constants for the cases shown in Figures 56a and 56b, the exponential term  $e^{-E/kt}$  is the major factor. Based on Equation (2), the collisional ionization rate constant in the case of Figure 56b will be enhanced by a factor of  $1.8 \times 10^5$  in comparison with that the case of Figure 56a. The experimental result in demonstrates the ionization enhancement of DLI over LEI is about 10<sup>2</sup> for the case of Figure 56a. Based on the rate equation approach, the ionization enhancement of DLI over determined by LEI is mainly the ratio of the photoionization collisional rate constant to the ionization rate constant following dve the laser excitation (in Chapter IV). Because the collisional ionization rate constant for the case of Figure 56b is a factor of  $1.8 \times 10^5$  larger than that for the case of Figure 56a, and the photoionization cross sections are on the same orders for these two cases (145), we would expect **COllisional** ionization to dominate is found as

experimentally.

### C-3 One- or Two-Photon Resonance Excitation

Similar results were obtained for the Li 2S - 3D Figure 56f), the power two-photon transition (see dependence of the dye laser gave a slope of 2 and the ratio of DLI/LEI was  $\sim$  1. This indicates that the ionization pathway is dominated by collisions as discussed in Section C-2. For the 2S  $\rightarrow$  2P one-photon transition of Figure 56e, the observed ionization enhancement of DLI to LEI was, surprisingly, more than three orders of magnitude. Also, indicated power dependence measurements that the ionization pathway was mainly due to a multiphoton process involving one photon from the dye laser and the other photon from the N<sub>2</sub> laser. The ionization mechanism is thus similar to that of Figure 56a. As noted previously the ionization enhancement of DLI over LEI is approximately determined by the ratio, from the excited intermediate state, of the photoionization rate constant to the collisional ionization rate constant. Based on Equation (2), the relative value of the collisional ionization rate constant for the cases of Figure 56a Na and 56e Li can be

estimated. The concentration  $x_j$  in Equation (2) is the same for these two cases, becuase the same composition flame was used. The collision cross section  $\sigma_{M^*}$ ,  $x_j$  (where  $M^*$  is the alkali atom in its first excited state) is approximately equal to  $\sigma_{M,x_j}$  (where M is in the ground state ). Kelly and Padley in flame experiments (161) and Johnston and Kornegay in shock tube experiments (204) have suggested that the collisional ionization process

$$M + x_j \rightarrow M^+ + e^- + x_j$$
 (a)

may be interpreted on the basis of three subreactions

$$M + x_{j} \stackrel{\stackrel{\sim}{\leftarrow}}{} M^{*} + x_{j}$$
(b)  
$$M^{*} + x \stackrel{\rightarrow}{\to} M^{**} + x$$
(c)

$$M^{+} x_{j} \rightarrow M^{+} + e^{-} + x_{j} \qquad (d)$$

where M and  $x_j$  are as defined previously; M<sup>\*</sup> is the analyte in its first excited state and M<sup>\*\*</sup> is the analyte in a higher excited state. The optical cross section for initial electronic excitation (step (b)) is about thousand-fold smaller than the ionization cross section for ionization steps (c) and (d) (161,203). Hence it is resonable to assume  $\sigma_{M^*, x_j} \sim \sigma_{M, x_j}$ . Kelly and Padley have determined  $\sigma_{Na}$ , Ar = 2700 Å<sup>2</sup> and  $\sigma_{Li,Ar}$  = 1200 Å<sup>2</sup>, as well as  $\sigma_{Na,H_2O}$  = 11000 Å<sup>2</sup> and  $\sigma_{Li}$ ,  $H_{2O}$  = 5500 Å<sup>2</sup> (161). The energy defect E is 3.04 ev for Na and 3.54 ev for Li; kT  $\sim$ 

0.18 ev for a 2100 K flame. Based on these data and Equation (2), the ratio estimation gives

$$\frac{K_{\rm Na}}{K_{\rm Li}} \approx 20$$
 (3)

where  $K_{Na}$  and  $K_{Li}$  indicate the collisional ionization rate constant for Na and Li, respectively. The photoionization rate constant R is equal to the product of the photoionization cross section  $\sigma_{phot}$ . and the photon flux (photons/sec.cm<sup>2</sup>) of the N<sub>2</sub> laser (153); i.e.

$$R = \sigma_{pho} \Phi \qquad (4)$$

The value of  $\sigma_{\rm phot.}$  for Na from the 3P state to the ionization threshold is 7.38 x  $10^{-18}$  cm<sup>2</sup> and  $\sigma_{\rm phot.}$  for Li from the 2P state to the ionization threshold is 15.20 x  $10^{-18}$  cm<sup>2</sup> (145). Thus, the ratio of photoionization rates gives

$$\frac{R_{\text{Li}}}{R_{\text{Na}}} \approx 2 , \qquad (5)$$

if identical  $N_2$  laser powers are assumed. therefore, comparison of DLI/LEI ionization enhancement between the cases of Figure 56a and 56e can be estimated as

$$\frac{\frac{R_{Li}}{K_{Li}}}{\frac{R_{Na}}{K_{Na}}} \approx 40$$
(6)

Experimentally this ratio is > 10. Thus this extimation gives an enhancement ratio of the same order of magnitude that obtained experimentally. When as the formalism outline in Section C-2 for Na (3S-4D) two-photon excitation is applied to Li, the collisional ionization rate constant from the 3D state (Figure 56f) is calculated to be 8 x  $10^4$  times larger than that from the 2P state (Figure 56e). This value is much larger than  $10^3$  for the measurement of the DLI to LEI ratio (in Figure 56e). Therefore, it is expected that collisional again ionization following the dye laser exctation dominates the case of Figure 56f. This is in agreement with the experimental results.

# C-4 <u>Na 3S - 5S Two-photon Absorption and 3P - 5S</u> <u>One-photon Absorption</u>

In order to obtain a measurable LEI or DLI signal upon 3S - 5S two-photon resonance excitation, the position of the electrode probes were adjusted to be as close to the laser-beams(s) as possible; otherwise no significant signal could be obtained. The DLI signal in this case (Figure 56c) is smaller and harder to obtain than that of the case in Figure 56b under similar experimental

conditions. The 5S level is lower by 0.18 ev than the 4D level which decreases the collisional ionization rate constant in case of Figure 56c by about a factor of three. This contribute somewhat to the experimental may difficulty. The dye laser power dependence plot shows the required slope of 2, and the DLI/LEI ratio is  $\sim 1$  for 3S + 5S case (Figure 56c. These results are analogous to the cases of Figure 56b and 56f. Based on Equation (2) the collisional ionization rate constant in the case of Figure 56c is estimated to be about 7 x  $10^4$  times larger than calculated for Figure 56a. Again, collisional that ionization is expected to predominate after 3S → **5**S resonance excitation (Figure 56c). The experimental result is consistent with this mechanism.

An interesting case is shown in Figure 56d, where the 3P level is thermally populated, and resonance excitation is provided by absorption of one dye laser photon to the 5S state. The DLI signal obtained under these conditions is shown in Figure 62; LEI (no N2 laser irradiation of the flame) produces essentially identically results. In both cases the expected slope of one is obtained from the plot of dye laser power dependence, as shown in Figure 63. Once again DLI/LEI $\sim$  1, demonstrates that collisional processes dominate the ionization step. The laser excitation involves only one photon, as in Figure 56a, and 56e; however, now the energy defect is sufficiently small that the effect of the  $N_2$  laser in case



Figure 62. Na ion spectra from DLI with 3P + 5S one-photon excitation, case (d) of Figure 56, 6154 Å indicates the ion peak induced by the 3  $P_{k_1} + 5S_{k_2}$  transition; 6161 Å is due to  $3P_{3/2} + 5S_{k_2}$ 

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Eigure 63. Dye laser power dependence of sodium ionization with one-photon absorption  $(3P_{3/2} + 5S)$ . The  $3P_{3/2}$ level is thermally populated.  $\Delta$  indicates DLI;  $\circ$  indicates LEI. The slpe of each line is one.

of Figure 56d is insignificant.

### D. Conclusion

As discussed above, it is clear that the energy defect between continuum and the resonantly excited state of the analyte has substantial influence on the ionization enhancement of DLI over LEI. When the resonant excited state is sufficiently close to the ionization threshold, the collisional ionization dominates photoionization following the dye laser excitation. As a result, neither the additional N<sub>2</sub> laser nor additional photons from the tuned dye laser make significant contribution to ion production under this condition, except for inducing more background, as discussed in Section C-1. ion The competition of collisional ionization and photoionization can be approximately gauged by the comparison of the collisional ionization rate constant and the photoionization rate constant from the resonantly excited state, based on the rate equation approach described in Chapter IV. Satisfactory agreement between calculated prediction and experimental observations is achieved.

Influence of the energy defect on the ionization process has also been observed by Smyth and coworkers, who noted that oxide molecules in a  $C_2H_2/air$  flame can be

either ionized collisionally or ionized by two photons resonant irradiation of a dye laser, depending on the energy defect between the ionization threshold and the state (16-18). resonantly excited The collisional ionization rate constant increases exponentially with decreasing energy defect. And when the energy gap is small, the multphoton ionization rate is not changed significantly upon the addition of N<sub>2</sub> laser radiation (see, for example, the case of Figure 56b, calculated in Section C-2) Moreover, it has been pointed out that the photoionization cross sections for some elements decrease the photon energy over the as ionization threshold increases (145, 205).These factors result in the domination of collisional ionization over photoionization when a higher energy level is selected for excitation.

In summary, it appears that if the resonantly excited state of the analyte in the flame is more than about 2.5 ev below the ionization threshold, then photoionization predominates over collisional ionization. Under such conditions, DLI offers distinct advantages over LEI in sensitivity for trace element analysis. The excited analyte absorbs a single photon from the N<sub>2</sub> laser (3371 Å = 3.6 ev) which raises it energy above the ionization threshold. Similar excitation into the continuum by the tunable dye laser above (LEI) would require multiphoton absorption of at least two (more likely three) dye laser photon, and thus would demand significantly higher dye

laser power than is required for DLI. An example of the sensitivity of DLI is given in Figure 64. A strong Li ion chloride solution with trace Li conta mination; however, no significant Li ion signal is detectable with LEI from the same NaCl solution. Figure 64. Spectra of (a) lithium DLI and (b) lithium LEI (x 200) with  $2S \rightarrow 2P$  excitation. The reagent is 100 µg/ml Nacl solution with trace Li contamination.



#### CHAPTER VIII

#### SUGGESTIONS FOR FUTURE DEVELOPMENT OF DLI

### A.Summary

Two main subjects have been investigated in the previous chapters: (1) flame and ion properties probed by DLI and (2) the relative merits of DLI and LEI techniques.

The first subject included flame temperature determination by DLI, the measurement of ion mobility and diffusion coefficients, and the measurement of ion life time with respect to the biasing voltage on the probes and the position of the ionizing sources (Chapter V). A current and voltage-dependent formulation has been derived to characterize the ion production by the lasers and to estimate the ion density in the flame (Chapter VI).

In the second subject, two theoretical models based on quantum mechanical methods (Chapter III) and rate equations (Chapter IV) have been studied to gain insight into the ionization processes, ion spectral and temporal profiles, the relationship between ionization and fluorescence, and the ionization enhancement of DLI over LEI. Finally, optimal use of DLI, based on the analyte's energy levels, has been suggested (Chapter VII).

### B. Proposal for DLI Development

# B-1 <u>DLI-diagnosis of Spectral and Temporal Information</u> Regarding Excited States

Most current research into OGE (the optogalvanic effect) in flames is related to ion production characteristics. However, the possibility of DLI or LEI providing information about excited state populations is worthy of exploration. The use of DLI to study excited state structure entails two steps, described below.

1. Spectral Characterization of Excited State Population

Molecular LEI developed at NBS has clearly revealed that the LEI spectra of oxide molecules were identical to the one photon absorption spectra from the ground state to the resonant intermediate state, and that the intensity and the resolution of LEI spectra were better than those from laser-induced fluorescence (17,18). Zare et al. reported OGE spectra of  $I_2$  in a discharge tube resembled the laser-induced fluorescence in both spectroscopic features and relative absorption probability (46). The resemblance of the LEI spectra in a discharge tube to the corresponding emission spectra was also reported (35). It appears possible to employ OGE as an alternative to optical spectroscopies (e.g. fluorescence) to identify discrete excited energy states of atoms and molecules in flames, and to investigate the oscillator strength for each resonance state. It is possible to imagine the tunable dye laser as a probe of the excited state location, and the N<sub>2</sub> laser as an efficient means of converting the excited state species into ions. The ion spectra thus provide information about discrete states, which is conventionally gained by absorption or emission of light.

The current development of OGE in flames still concentrates on the low-lying levels of atoms and molecules, but the scope of OGE in gas discharges has been extended to the high-lying levels (Rydberg states). Five detection methods of Rydberg states usually employed are fluorescence, field ionization, collisional ionization, photoionization and OGE (Chapter I). The last four methods ionization are related to spectroscopies and show superiority to the fluorescence method. Dalsart et al. employed the OGE method to obtain new data on Kr have Rydberg states, which did not appear with the field ionization method (57,58). Therefore, discovery and classification of Rydberg states of atoms in flames with high resolution via OGE spectroscopy is possible, and worthy of to development. As discussed in chapter VII, DLI

may lose its sensitivity and act as normal LEI (i.e. single laser in radiation) when the dye laser is tuned to resonance with transition to higher energy levels. Therefore, double resonance OGE ("stepwise excitation") with two high resolution tunable lasers (the second laser being used as a probe) may provide a better tool to investigate atomic Rydberg states.

2. Temporal Studies of Excited State Population (Lifetime Measurement by DLI)

From the Na energy scheme shown in Figure 65a, one obtains the ionization rate equation as

$$\frac{dn_{i}}{dt} = (R\phi + r\psi + k) n_{f} - K_{ni}, \qquad (1)$$

where  $n_i$  and  $n_f$  are the ion density and the excited state population density, respectively; R and r are photoionization cross sections for one photon ( $N_2$  laser) and two photons (dye laser), respectively, starting from the excited state, and  $\phi$  and  $\psi$  indicate the photon flux of the  $N_2$  laser and the dye laser, respectively. K is the relaxation rate constant of the ion and k is the collisional ionization rate constant. The one-photon ( $N_2$ -laser) photoionization process from the excited state was found to dominate the ionization pathway (Chapter III, IV and VII), if the alkali element was excited to its first excited state. Therefore,  $r\psi$  and k may be considered

- Figure 65. Partial energy level diagram of sodium. The dye is tuned to resonance with the 3S + 3P transition. Na<sup>+</sup> may be induced by one-photon absorption of the N<sub>2</sub> laser, absorption of two additional photons from the dye laser, and collisional energy exchange. K indicates the relaxation rate constant from the continuum, including all types of relaxation.
  - b. Elock diagram of an experimental set-up for temporal profile measurement by DLI. A is the N<sub>2</sub> laser; E is a dye cuvette in which the second laser beam is produced; C is the flame system;
    D are flat mirrors; E is two pairs of flat mirrors used to variably delay the light path of the N<sub>2</sub> laser.



negligible in comparison with  $R\phi$ . under these conditions. If the two additional conditions,  $R\phi = n_f >> Kn_i$  and the  $N_2$ laser profile is a  $\delta$  function are assumed, Equation (1) can be integrated as

$$n_{i} = \int R \phi(t) n_{f}(t) dt$$
  
=  $\int \delta(t) n_{f}(t) dt$   
=  $n_{f}(0)$  (2)

By using flat mirrors to optically delay the  $N_2$  laser, the temporal profile of the beam may be lag adjusted by T nsec with respect to that of dye laser. Substitution of lag-time T into Equation (2) gives

$$n_{i} = \int \delta(t-T) n_{f}(t) dt$$
  
=  $n_{f}(T)$  (3)

where  $n_f(T)$  indicates the population of the excited state at time T. By varying the lag-time T successively, one may obtain a set of data  $n_f(T_j)$  against  $T_j$ , and the lifetime of fluorescence can be determined from the temporal profile. DLI measurement of the lifetime of the excited population possesses all the advantages of the DLI technique. In addition, two special advantages are provided here: (1) the temporal profile of the excited population is obtained by an ionization method, instead of conventional photon spectroscopy; (2) a slow ion detector

is used, instead of a fast photon detector.

The possiblity of DLI-provision of spectral and temporal information about excited states may result in the superiority of DLI to other optical spectroscopies related to discrete states, not only in showing an extreme sensitivity to trace elements but also in providing more information about the dynamics of processes involving continuum and discrete levels.

## B-2 Re-examination of Sensitivity and Selectivity of DLI

As discussed in chapter VII, in comparison with normal LEI, under certain circumstances DLI shows much higher sensitivity to ion detection, because the photoionization process prevails from the resonantly excited state DLI does not show better sensitivity in separating two elements with almost identical energies of their resonantly excited states or with low ionization potentials, because the  $N_2$  laser may ionize both elements simultaneously by one photon absorption. Some possible ways to improve DLI selectivity are:

(1) by choosing different energy levels as intermediate excited states, but then DLI may lose its prevailing sensitivity as higher excited states are chosen.

(2) by using time-delay (i.e. the  $N_2$  laser pulse is lag adjusted with respect to the dye laser pulse) to decrease the excited population of the interference matrix before irradiation with the  $N_2$  laser; this method is restricted to long liftime excited states of analytes.

(3) by using a double resonance OGE spectroscopy with two tunable dye lasers; this may allow both high sensitivity and high selectivity to ion detection through the choice of various double-resonance laser combinations.

## B-3 Saturation Dual Laser Ionization

Based on the rate equation approach described in Chapter IV, "saturation DLI" may be achieved with power densities of the dye laser of similar order of magnitude to those which provide saturation laser-induced fluorescence. Saturation ionization spectroscopies have been widely developed in non-flame systems; their advantage is independence of laser power (206).

## B-4 DLI in Vapor Cells Versus DLI in Flames

DLI may also be applied in a vapor cell. experimental set-up of DLI in a vapor cell is illustrated in Figure 66. A schematic preliminary experiments were carried out, and it was possible to obtain an ion signal, as shown in Figure 67.

Several advantages of DLI in a vapor cell exist such as:

(1) it is easy to control and simplify the matrix in a vapor cell.

(2) it is possible to separate multiphoton ionization from collisional ionization by controlling the pressure in the cell.

Several disadvantages (in relation to the alkali elements), such as dimerization, oxide and hydroxide conta minations, and light scattering by the quartz windows, also exist. The investigation of DLI in vapor cells may complement the studies of DLI in flames, and provide additional important fundamental phenomena.

Figure 66. Elock diagram of the experimental set-up for DLI in a vapor cell. The cell and windows are quartz, and the electrodes are nichrome plates. The ion current from the center electrode is input to a boxcar averager. The entire cell is placed in a furnace (indicated by the dashed line), which is maintained at a controlled temperature in the 350-400 °C range.





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may have been obtained under atmospheric conditions. Figure 67. The ion signal of Na in aguartz cell, induced by transition. The initial pressure inside the cell DLI with the dye laser tuned across the 3S + 3P was found to have leaked. Hence the ion signal

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APPENDICES

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#### APPENDIX A

# TWO-STEP LASER-ASSISTED IONIZATION OF SODIUM IN A HYDROGEN-OXYGEN-ARGON FLAME\*

## A. Introduction

Laser enhanced ionization (LEI) in flames and been observed with various experimental plasmas has designs (4,20,51-53,64,207,208).In the usual LEI experiment, ionization results from the absorption of a resonant laser photon followed presumably by collisions of the excited atom with flame gas combustion products (4,20). Absorption of a resonant laser photon with an energy E reduces the effective ionization energy and increases the ionization rate (4,20) by a factor of exp (E/kT), where T is the flame temperature; this factor can easily be on the order of 10<sup>4</sup>. In this paper we report a relatively simple and inexpensive method for producing laser-assisted ionization in a flame. The method utilizes a two-step process, as suggested by various authors (22,23). The first step is the absorption of a resonant laser photon by an atom in the ground state, followed by the absorption of an off-resonant photon by the atom in the excited state. The sum of the energies of the two photons is such that it exceeds the ionization energy of the atom.

The fact that two laser photons are being used to ionize the atom does not necessarily mean that the ionization proceeds through a straight-forward two-step process. It has recently been proposed that photoionization might be collision assisted (209). Since collisions are frequent in a flame at atmospheric pressure, this latter possibility was investigated, and some experiments are presented to elucidate the predominant ionization mechanism.

### B. Experimental

The experimental setup is shown in Figure 68. A relatively cool (1800 K)  $H_2-O_2$ -Ar flame is burned from a circular Mékér burner and shielded by a mantle flame of the same composition to prevent the entrainment of air. Sodium is introduced into the inner flame by nebulizing a sodium salt solution with a pneumatic nebulizer driven by the argon stream. A homemade tunable dye laser of the Hansch design (103), using Rhodamine 6G as a dye, is

- Figure 68. Experimental arrangement for simultaneous observation of laser-assisted ionization and laser induced fluorescence.
  - (a) Overall view. B, boxcar; DL, dye laser; F, flame; L, lens; M, mirror; O, oscilloscope; PL, pump laser; PM, photomultiplier; R, x-t recorder; S, signal; T, uv rejecting filter; TL, trigger line.
  - (b) Detailed view of probes and laser beams. IF, inner flame; OF, outer flame; P, probe; R, Load Resistor; S, signal. Dimensions are not to scale. The waist diameter of the laser beams is of the order of 0.1 mm; the distance between the probes is a few mm; the diameter of the inner flame is approximately 15 mm.



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pu WI la ар th 05 us Om Wa Ie Mo Was the Po in The pu of the las bia The sta irr Ion loa pumped by a N<sub>2</sub> laser (Model 0.5 - 150, NRG, Inc., Madison, WI). The pulse duration is 5 ns for both lassers. The dye laser beam is focused in the center of the flame, approximated 2 cm above the burner head, well away from the combustion region. The width of the spectral profile of the dye laser at a wavelength of 5890 Å was measured by using the fluorescence excitation profile as discussed by Omenetto et al. (137) and fround to be  $0.7\pm0.1$  Å. The wavelength of the N<sub>2</sub> laser is 337 nm. Output powers were measured with pyroelectric power meter (Model J3 - 05, Molectron Corp., Sunnyvale, CA). Part of the N2 laser beam was split off from the pumping beam and also directed into the flame, where it was focused with a quartz lens. Positioning devices carrying mirrors and lenses facilitate in maximizing the spatial overlap of the two laser beams. The degree of temporal overlap between the two laser pulses can be varied by changing the optical path lengths of one or both lasers. The path lengths were adjusted in these experiments for maximum temporal overlap of the two lasers at the burner.

The ionization signal was detected with a pair of biased nichrome wires, which had a diameter of 0.7 mm. These probes were mounted on micrometer-driven translation stages and located in the immediate neighborhood of the irradiated region but were not irradiated themselves. Ionization signals were measured across an interchangeable load resistor in the probe circuit. The signals from the

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probes were usually processed by a boxcar averager with gated integrator (Model 162 - 164, Princeton Applied Research, Princeton, NJ) and read out by an x-t recorder. A photomultiplier (RCA 1P28), wired for last pulse processing, monitored the fluorescence from the 3P + 3S transitions of Both the ionization sodium. and the observed fluorescence signal can be on a storage oscilloscope (Model 564 Tektronix, Inc., Beaverton, OR). Appropriate shielding prevents stray light due to the dye laser from entering the photomultiplier. A UV rejecting filter in front of the photomultiplier was used to cut out stray light due to the N, laser. Two rf chokes, consisting of several wire turns around a ferrite core, were soldered into the high-voltage power line of the N<sub>2</sub> laser; both the laser and the chokes were put inside a grounded Faraday cage, consisting of 0.5 mm copper plating. These measures substantially decreased the rf noise from the N2-laser discharge.

## C. Results and Discussion

Experiments were performed to measure the enhancement of the ionization signal with both the dye laser and the  $N_2$  laser irradiating the flame over the signal obtained with the dye laser alone. For these

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experiments, the dye laser was tuned to the Na( $3S_{1/2} \rightarrow$  $3P_{3/2}$ ) transition and a Na concentration of 12 g/mL was nebulized into the flame. The laser peak powers were of the order of 40 and 100 kW for the dye laser and the split part of the N<sub>2</sub> laser beam, respectively. off The ionization and signal was integrated over time. With the dye laser only, an ionization signal of 9.0 mV was obtained; with both lasers the ionization signal increased to 1.3 V. No signal was obtained with the  $N_2$  laser alone. The enhancement factor was thus 144 for these experiments. The exact enhancement factor depends on the configuration of the beams and the probes, the intensities of the beams, and of the composition of the flame. We observe that this factor can be improved by moving the probes closer to the irradiated region. The latter manipulation, however, tends to affect the reproducibility of the experiment because of the more critical alignment. Moreover, when the lasers irradiate probe surfaces, nonspecific occurs, which is possibly due to electrons being liberated from the probe material by laser photons or due to off-resonant multiphoton ionization of atoms and molecules in particle sheaths which might envelop the probes.

To investigate the analytical utility of the two-step ionization technique, we measured the ionization signal and the degree of ionization as a function of the sodium solution concentration. The reaults are given in Figure 69. The dye laser was tuned to the  $Na(3S_{1/2} +$ 

Figure 69. Ionization siganl ( $\circ$ ) and ratio of ionization signal to sodium solution concentration ( $\Box$ ) vs. sodium solution conentration; both lasers are irradiating the probed volume. The dye laser was tuned to the  $3S_{\frac{1}{2}} + 3P_{3/2}$  (589.0 nm) transition.

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 $3P_{3/2}$ ) transition, the N<sub>2</sub> laser irradiated the same flame volume, and the time-integrated ionization signal was measured. The analytical curve shows a nearly constant slope of 1 over more than 2 decades of solution concentration, and the lowest concentration detected was 0.1 µg/mL. From the fact that a slope of 1 occurs it can be concluded that associative ionization is not present to any significant extent, since two sodium atoms are required ( $2Na^* + hv + Na_2^+ + e^-$ ) (210,211) and a slope of 2 would result. The nonlinearity of the curve in Figure 69 may be due to a decrease in the ion collection efficiency caused by the formation of charge sheaths (8) or by ion-electron recombination.

A plot of the ratio of the ionization signal to the sodium solution concentraiton vs. the sodium solution concentration has been previously related to the degree of ionization (4). Such a plot, shown in Figure 69, also exhibits nonlinearity. This phenomenon has been observed with a different ionization scheme but in virtually the same flame (4). That the deviation from linearity in Figure 69 was not due to nebulizer characteristics was checked by plotting the thermal emission from the Na(3P  $\rightarrow$ 3S) transitions against sodium solution concentration. The latter plot showed deviations from linearity in a concentration range well above that of Figure 69, due to the combined effect of self-absorption and decreasing atomization efficiency with increasing concentration.

Profiles of the ionization and fluorescence signal were obtained by tuning the dye laser across the Na( $3S_{1/2}$ +  $3P_{3/2}$ ) transition and are shown in Figure 70. The sodium solution concentration nebulized into the flame was 12 µg/mL. The difference in the full widths at half-maximum (fwhm) which is evident from the profiles of Figure 70, has been observed in a related experiment by van Dijk et al. (4) where a flashlamp laser was used.

The fluorescence excitation profile in Figure 70 essentially represents the spectral laser profile because the width of the Na( $3P \rightarrow 3S$ ) transitions is known to be approximately 70 mA in our flame (212), which is small compared to the observed width. Saturation of the  $Na(3S_{1/2})$ +  $3P_{3/2}$ ) transition hardly affects the latter conclusion, since the broadening of the excitation profile depends on the square root of the natural logarithm of the dye laser power (137) and is therefore a weak function of this power. The measured fwhm of 0.7 A of the fluorescence excitation profile is consistent with the value which we obtained when using a monochromator to resolve the spectral laser profile. Broadening of the ionization profile might be related to saturation of the (8), laser-excited level, space charge effects and possibly recombination (4).

On a microsecond time scale the onset of the recombination might occur and this might partially account for the difference in widths observed in the profiles of

Figure 70. Profile of ionization signal ( $\Box$ ) and fluorescence (O) obtained by scanning dye laser across the  $3S_{\frac{1}{2}}$  to  $3P_{3/2}$  (589.0 nm) Na transition. FWHM = 0.7 Å for fluorescence profile and 1.5 Å for ionization profile. Sodium solution concentration =  $12\mu g/m l$ , probe voltage = 400 V.



noted by Muller et Figure 70 (4). As al. (213).appreciable charge densities are needed to give rise to noticeable recombination on a microsecond time scale. We hypothesis offer the following to account for recombination under our experimental conditions: the possible existence of charge sheaths around the probes might partially nullify the electric field between the probes and lead to an increase in the contribution of difussion to the motion of the charges in the "field-free" region. Therefore, a significant numbers of ions might be able to overcome the repulsive field at the positive probe. These ions have a higher probability of being neutralized because of the electron sheath enveloping the latter probe. An analogous reasoning applies to the electrons. As the charge densities in the sheath are higher than in the surrounding plasma, the recombination rate will also be higher near the sheaths. The fact that space charges diminish the field might also decrease the collection efficiency of the probes and give rise to broadening of the ionization profile.

We investigated the dependence of the ionization and fluorescence signals on small variations in flame gas composition. The influence of changing the oxygen content on the signals is quite noticeable but different for the excited-state population and the ionization. However, the ratio of the ionization signal to the fluorescence signal shows only a weak dependence on the O<sub>2</sub> concentration. The

ratio of the ionization signal to the fluorescence signal is proportional to the degree of ionization  $\beta$ , provided  $\beta$ is small and the  $3S_{1/2} - 3P_{3/2}$  transition is saturated

$$\beta \equiv [Na^{+}]/([Na^{+}] + [Na]) \simeq [Na^{+}]/[Na^{*}] \propto i/F$$
(1)

where  $Na^{\pi}$  is the density of the excited sodium atoms, i=ionization signal, and F=fluorescence signal.

In an analogous experiment, where we varied the argon content of the flame, a similar weak dependence was observed, as is evident from the curves in Figure 71. From these experiments one can conclude that if the degree of ionization is low, the discrete to continuum step is predominately photon absorption and thus affected only slightly by collisions with 0, or Ar. On the other hand, if the degree of ionization is high, this conclusion does not necessarily hold because a variation in the ionization rate will have little influence on for close to unity. Rough calculations indicate that the degree of ionization within the laser irradiated volume may indeed be quite high. When the discrete to continuum step is brought about solely by collisions, the dependence of i/F on the  $O_2$ concentration in the flame is much more pronounced (4, 214).

Changing the voltage across the probes results in a change in the ionization signal, as is shown in Figure 72. For this experiment we used various sodium solution

Figure 71. Dependence of ionization and fluorescence signals on Ar content of flame. The dye laser was tuned to Na( $3S_{\frac{1}{2}} + 3P_{3/2}$ ) transition; the sodium concentration was 12 µg/ml.

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- Fluorescence signal plotted vs. Ar flow
- Ionization signal plotted vs. Ar flow
- Ratio of ionization-to-fluorescence signal plotted vs. Ar flow.



- Figure 72. Dependence of ionization signal on probe voltage for various sodium solution concentrations. The dye laser was tuned to the 3S<sub>12</sub> + 3P<sub>3/2</sub> transition. A dc component in the signal, probably due to thermal (non-laser) ionization, was eliminated with a capacitor in the signal line.

  O - Sodium concentration = 10 ppm
  - $\Delta$  Sodium concentration = 10 ppm  $\Box$  - Sodium concentration = 1 ppm  $\Box$  - Sodium concentration = 100 ppb



concentrations, and the dye laser was tuned to the  $3S_{1/2}$  to  $3P_{3/2}$  transition. With increasing voltage the curves are seen to level off, especially those of the higher concentrations. The decreasing slopes indicate that the current drawn from the plasma approaches saturation, which means that with high voltages eventually all the available charge carriers in the probed region are being collected.

A check as to the transport mechanism can be obtained by plotting the measured decay time of the ionization signal vs. the reciprocal of the applied probe voltage  $2\phi_{p}$ . According to Equation Al3 of the Appendix, such a plot is expected to yield a straight line: indeed we found this to be the case. From the slope of this plot we calculate, using Equation Al3 with 2L = 2.8 mm, that the ionic mobility  $\mu_{i_i}$  is on the order of 20 cm<sup>2</sup> v<sup>-1</sup>s<sup>-1</sup>. we assume that the additional decay time  $\tau_{a}$ , When introduced by the circuitry, especially the load resistor (= 100 k $\Omega$  ), is simply added to the characteristic decay time  ${\mathcal T}_{{\mathbf i}}$  , we find from the intercept of the plot of decay time vs. inverse probe voltage that  $\phi_{\mu}$  = 20 s. Hence the stray capacitance of the circuitry is 200 pF, in resonable agreement with estimates based on cable length and input capacitance of the apparatus.

Using the relation  $\mu_i = qD/(kT)$ , where q = elementary charge, D = diffusion coefficient, k = Boltzmann's constant, and T = flame temperature, we calculated the order of magnitude of  $\mu_i$  from measurements

2.73

of the diffusion coefficient in flames by Ashton amd Hayhurst (185) and found our result to be within the range of the latter authors. Electronic mobilities are expected to be much larger because of the difference in mass between the ions and the electrons (215). When we calculate the decay time under the assumption that diffusion is the predominant transport mode, we find, using  $\tau_{diff} = (2L/\pi)^2/D$  (182), and  $D = \mu_i kT/q, \tau_{diff}$  is of the order of several milliseconds and is therefore much our observed values. larger than Two conclusions pertaining to the particular conditions of our experiment can be drawn from these experiments:

(1) The predominant transport mechanism is drift due to the electric field of the probes.

(2) The current is limited by the ions.

It follows from our measurements and from Equation Al3 that the actual decay time of the charge cloud is several microseconds. Τn order to eliminate the contribution of the circuitry to the decay time constant, we plotted this constant vs. the value of the load resistor. These latter measurements support our observation that  $\tau_i$  is of the order of a few microseconds, since for low values of  $R_1$  the observed time constant becomes independent of R1.

The temporal dependence of the ionization signal was measured with a load resistor  $R_1$  of 5 k  $\Omega$ . The peak amplitude  $V_0$  of this signal was 12 mV and the decay was

close to exponential with a time constant  $\tau$  of 7.9  $\pm$  0.2  $\mu$ s. An estimate of the total number of ions collected in this pulse follows from

$$v_0 \int_0^\infty e^{-t/\tau} dt = NqR_1$$
 (2)

where q is the elementary charge. From these results N is found to be approximately  $10^8$  Note that the exponential decay is consistent with Equation A4 of the Appendix.

By tuning the dye laser across the  $3S \rightarrow 4D$ two-photon transition of sodium and using a 100 uq/mL sodium solution concentration, the profile shown in Figure 73 was obtained. The signal from this transition is weaker than the signal of a 3P - 3S transition when referred to the same solution concentration. The peak observed with dye laser only is probably due to collisional the ionization proceeding from the 4D level (4,10). The fact that very little enhancement of the latter peak occurs N<sub>2</sub> laser is present might mean that the when the ionization induced by the dye laser and the collicions is nearly complete, or alternatively, that the cross-section for photoionization from the 4D level to the continuum is small. The continuum signal observed with both lasers irradiating the flame disappears when the dye laser is blocked or when the N<sub>2</sub> laser is blocked. This indicates continuum signal is due to off-resonant that the two-photon ionization by both lasers.
- Figure 73. Ionization profiles obtained by scanning the dye laser across the Na(3S + 4D) two-photon transition; center wavelength = 5787 Å,  $R_{\ell} = 50 \ k\Omega$ ,  $2\Phi_p = 100 \ V$ ; sodium solution concentration = 100 µg/ml.
  - (a) Upper trace:  $N_2$  laser beam interrupted Lower trace: both the  $N_2$  laser beam and the dye laser beam operative.

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(b) Detailed profile.



## D. Conclusions

We have shown that ionization of seed atoms in a flame can be achieved relatively simply by irradiating the atoms simultaneously with one resonant and one off-resonant laser pulse, both of which have a duration of a few nanoseconds. From the experiments conducted we conclude that the predominant mechanism for ionization is the Na(3P) level proceeding from two-step photoionization; in the case of population of the Na(4D) level, collisions cause the excited atom to ionize. The described method to measure ion mobilities has been tested and been found to yield a value consistent with previous results.

Although the detection limits by the two-step method are not as low as those obtained by normal LEI (8), it is expected that perfection of this method will improve these limit. Feasible improvements are: using a slot burner and extended probes runing parallel to the laser beam for several inches to increase the collection efficiency of the probes; using an ultrasonic nebulizer instead of pneumatic nebulizer our to increase nebulization efficiency; narrowing the bandwidth of the dye laser to increase its spectral irradiance.

## E. Appendix

In this appendix we develop expressions for the mobility controlled ion density in a flame. As an approximation to our experimental conditions, we consider two parallel plane probes at a distance 2L from each other, with a voltage difference  $2\phi_p$  applied to them by an external source. The probes are located inside the flame and the charge density is assumed to be uniform throughout the space between the probes when the applied voltage is zero.

We are interested in the case in which the distribution of the ions is primarily determined by the electric field; consequently, we neglect here diffusion, the overall movement of the flame gases, recombination, and ion production. The continuity equation for the ion density then reads

$$\partial \mathbf{n}_{i} / \partial t = -\mu_{i} \nabla (\mathbf{n}_{i} \mathbf{E})$$
 (A1)

where  $\mu_i$  denotes the ionic mobility and  $\check{E}$  denotes the electric field. If the contribution of the laser-induced charges to the field  $\check{E}$  is small, the  $\check{E}$  is nearly constant during a laser pulse. The latter assumption allows us to

separate variables as follows

$$n_{i}(x,y,z,t) = N_{i}(x,y,z)f_{i}(t)$$
 (A2)

Sustituting Equation A2 into Equation Al gives

$$\frac{1}{f_{i}(t)} \quad \frac{\partial f_{i}}{\partial t} = \frac{\mu_{i}}{N_{i}} \quad \nabla (N_{i}E)$$
(A3)

Since the left-hand side of Equation A3 depends on t only and the right-hand side on the spatial variables only, we set both sides equal to a constant  $-1/\tau_i$ . The solution for  $f_i(t)$  is found to be

$$f_{i}(t) = e^{-t/\tau}$$
 (A4)

The equation for the steady state can be written as

$$\nabla (N_{i}\tilde{E}) - N_{i}/(\mu_{i}\tau_{i}) = 0$$
 (A5)

Using the identity

$$\nabla (\alpha A) = \alpha \nabla A + A \nabla \alpha$$
 (A6)

where  $\alpha$  and A represent differentiable but otherwise arbitrary scalar ( $\alpha$ ) and vector (A) functions of the spatial coordinates, Equation A5 becomes

$$N_{i}\nabla\tilde{E} + \tilde{E}N_{i} - N_{i}/(\mu_{i}\tau_{i}) = 0$$
 (A7)

If we assume that the field E is nearly uniform throughout the probed region, then

$$E = - \Phi_{p}/L \tag{A8}$$

If our attention is restricted to the one-dimensional case, then substitution of Equaiton A8 in A7 gives

$$\partial N_{i} / \partial x = -N_{i} L / (\Phi_{p} \mu_{i} \tau_{i}) .$$
 (A9)

Hence

$$N_{i} = n \exp[-xL/(\phi_{p}\mu_{i}\tau_{i})], \qquad (A10)$$

where n is a constant of integration. Thus, the ion density is highest near the negative probe and decreases in the direction of the positive probe (located at x =+L). Identifying  $\tau_i$  with the characteristic time it takes for an ion to drift from x = 0 to x = -L

$$L = -v_{i}\tau_{i}$$
(A11)

where  $v_i$  is the average drift velocity. In the limit of a low, uniform field

$$\mathbf{v}_{\mathbf{i}} = \boldsymbol{\mu}_{\mathbf{i}} \mathbf{E} \tag{A12}$$

Combining Equation A8, All, and Al2

$$\tau_{i} = L^{2} / (\mu_{i} \Phi_{p})$$
 (A13)

establishes a relation between the characteristic decay time and the ionic mobility in terms of the distance between the probes and the applied potential. Using Equation AlO and Al3

$$N_{i} = n \exp(-x/L) \qquad -L < x < L \qquad (A14)$$

which agrees with the solution found for the so-called plasma-capacitor in the limit of low charge density (216). Due to the absence of the diffusion term in Equation A5, the charge density does not obey the boundary conditions  $N_i(\pm L) = 0$ .

\*Obtained jointly with C.A. van Dijk and F. M. Curran.

## APPENDIX B

## PHOTOIONIZATION CROSS SECTION BY QUANTUM DEFECT METHOD

The quantum defect method has been used in the calculation of photoionization cross sections. This method uses interpolated or extrapolated quantum defects to determine the asymptotic forms of atomic wave functions (100,205,217). In this appendix, some related parameters are calculated by simple numerical methods and compared with the original work by Peak (100). These parameters can be substituted into a general formula to calculate atomic photoionization cross sections.

The equations used in reference (100) are summarized below. The notation is identical to that of the original work.

The initial bound radial function P for the nlSL electron is

$$P_{\nu\ell}(\mathbf{r}) = z^{\frac{1}{2}} K(\nu, \ell) (2\rho/\nu) e^{-\rho/\nu} \sum_{t=0}^{t} b_t(\nu, \ell) \rho^{-t} , \qquad (1)$$

where  $\rho = zr$  and  $\nu$  is called the effective quantum number

and defined by  $\varepsilon v^2 = z^2$  ( $\varepsilon$  is the energy, measured in Rydbergs, required to remove the nl electron, and z is the residual charge and equal unity for neutral atoms). The continuum function  $G_{k'2}$  (r) is defined by

$$G_{k'l'}(r) \sim k'^{-\frac{1}{2}} \sin \left[ k'r - \frac{1}{2} l'\pi + \frac{z}{k'} \ln (2k'r) + \arg \Gamma \left( l' + 1 - \frac{iz}{k'} \right) + \pi \mu' \right], \qquad (2)$$

where  $k'^2 = z_{\epsilon}^2$  ' denotes the energy in Rydbergs of the ejected electron, and  $\mu$  ( $\epsilon'$ ) is the extrapolated quantum defect for the n'l'S'L' series. The quantum defect  $\mu'$  for the n'l'S'L' series is defined by  $\mu' = n' - \nu'$ .( n' is the principal quantum number and  $\nu'$  is the effective quantum number for the n'l'S'L' series.) Consequently, matrix element g ( $\nu$ , l;  $\epsilon'$ l') is written in the form:

$$g(\nu, \ell; \varepsilon', \ell') = \frac{z^2}{\nu} \int_0^\infty P_{\nu \ell}(r) r G_{k' \ell'}(r) dr$$
$$= f(\nu \ell; \varepsilon' \ell') \cos \pi \mu' + h(\nu \ell; \varepsilon' \ell') \sin \pi \ell'$$
(3)

or

$$g(v,l;\varepsilon'l') = \frac{B(vl;\varepsilon'l')}{\xi^{2}(v,l)} \cos \pi [v + \mu'(\varepsilon') + \chi(vl;\varepsilon'l')]$$

(4)

$$B(vl;\epsilon'l') = \xi^{\frac{1}{2}} (f^{2} + h^{2})^{\frac{1}{2}}$$
(5)

and

$$\pi (\nu + \chi) = \arctan (-h/f)$$
(6)

The photoionization cross section can be derived as

$$a_{v}(\varepsilon',v) = \frac{4\pi\alpha a_{0}^{2}}{\sqrt{2}}\left(\frac{z^{2}}{v^{2}}+z^{2}\varepsilon'\right)\sum_{\substack{k=\ell+1\\ k=\ell+1\\ \ell=\ell+1\\ \ell=$$

or

$$a_{\nu}(\varepsilon',\nu) = 5.44909 \times 10^{-19} \frac{\nu}{z^{2}\xi(\nu,\ell)} (1 + \varepsilon'\nu^{2})^{3} \times \frac{\Sigma}{\ell^{2}\xi(\nu,\ell)} \left[G(\nu\ell;\varepsilon'\ell')\cos\pi(\nu + \mu'(\varepsilon') + \ell'=\ell+1)\cos\pi(\nu\ell;\varepsilon'\ell') - 1\right]^{2}$$
(8)

where

$$G(\nu l; \varepsilon' l') = \left(\frac{\pi}{2\nu}\right)^{\frac{1}{2}} \left(1 + \varepsilon' \nu^{2}\right)^{\frac{1}{2}} B(\nu l; \varepsilon' l')$$
(9)

and the coefficient  $C_1$ , is defined in reference (205).

Table 5 shows a comparison of  $G(\nu l; \epsilon' l')$  and  $\chi(\nu l; \epsilon' l')$  values calculated here with Peach's results. The difference of numerical methods employed here from those in reference(100) lies in the DVERK( from DMSL routine library), which is used in calculating the continuum function G, and the DCADRE used for the matrix element g. With the obtained G and X values and Equation (9), the photoionization cross sections can be estimated.The Fortran program is listed below.

a'(cm<sup>2</sup>) G(v,l;e',l')  $\chi(v'l;\epsilon',l')$  $v; \varepsilon' l = 1$ (Rydberg) and this work Peach this work Peach this work Q. 0.299 v = 3;l'= 2 3.141 3.154 0.301  $1.759 \times 10^{-19}$ -0.314 v = 0.4l'= 0 1.252 1.297 -0.312 0.225 v = 2;l'= 2 2.731 2.730 0.226  $1.176 \times 10^{-18}$ 0.995 0.996 -0.304 -0.300 v = 0.1 $\ell = 0$ 

Table 5. Comparison of Parameters for Photoionization Cross Section Calculation

≠EQR	
	PROGRAM GUMDEF(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
	COMMON V(10) EI(10) LEIKEVIMEPYI(22) HYI(22) XXEFFYI(20) HHYI(20)
	REAL I
	XX=-0.08
	AERR=1.01=5. DEPD=0.
	3=22.
	C=50.
	V(T) = T
	VIM=V(I)
	EIK=C.1
	ASUM=U. DG 460 II=1.3.2
	L=IL-1
	CALL WKB(EIK,L,F,H,DF,DH)
4.0	WK115(594U) F949UF9UH FORMAT/2K,WF-W,F12,4,2X,WH-W,F12,4,2X,WDF-W,F12,4,2X,WDH-W,F12,4)
7,0	CALL FDIF(F+DF+FYI)
	AIN=DCADRE(FNLAF, A, B, AERR, RERR, ERROR, IER)
100	WRITE(S9100) L9AIN9ERROM9IER FORMAT(2Y,NI-N,T1,2Y,NATN-N,F11,A,FY,NFPPOP-N,F9,3,FY,NTFP-N,F3,1)
	CALL HDIF (H • DH • HYI • HHYI)
	BIN=DCADRE(FNLAH+A+B+AERR+RERR+ERROR+IER)
0.2.4	WRITE(59200) BIN9ERROR9IER Formation and the fill a system for a first at the filles
2.3	CIN=DCADRE (WKBF•C•D•AERR•RERR•ERROR•IER)
	WRITE(6,550) CIN, ERROR, IER
550	FORMAT(5X, "CIN=",E11.4,5X,"ERROR=",E8.3,5X,"IER=",F3.1)
	WRITE(5+250) DIN+ERROR+IFR
250	FORMAT(5x, "DIN=", E11.4, 5x, "ERROR=", E8.3, 5x, "IER=", F3.1)
	FDW=AIN+CIN
	HUW=BIN+JIN CALL DEFECT(XX)
	BM=SQRT(1.+(2./I++3)+DEFECT(XX))+SQRT(FDW++2+HDW++2)
	XAN=(ATAN(-HOW/FDW))/3.1416-I
	G=SGRT(S+1416/(2*1))*((1+E1K*(1**2))**2)*BM WRTTF(S+300) G-XAN
300	FORMAT(10X+2HG=+E10+4+10X+4HXAN=+E10+4)
	CL=2./3.
	IF(Letded) CL=Le/Se CALL DFFFCT(C_)
	AV=(5.44909E-19)*(I**3)/(1+(2./I**2)*DEFECT(XX))*
	*(1.+EIK*(I**2))**(-3)*CL*((G*COS(3.1415*(I+2.67+DEFECT(0.)*
	*EIK+XANJJJ**2) A SHM=ASHM+AV
400	CONTINUE
-	WRITE(5,700) VIM.EIK.ASUM
799	FORMAT(10X+2HV=+F4+1+5X+3HEP=+F4+1+5X+5HASUM=+E10+4) STOP
	ËND

1?

```
SUBROUTINE WK3(EIK+LP+F+H+DF+DH)
DIMENSION FI(10)+HI(10)
        R=21.6

D0 12 I=1.6

C=LP*(LP+1.)

W=EIK-C/R**2+2./R

DW=2.*C/R**3-2./R**2

DDW=J.625*C*(W**(-2.25))*DW/(R**3)-0.625*(W**(-2.25))*DW/(R**2)

S+1.5*C*(W**(-1.25))/(R**4)-W**(-1.25)/(R**3)

CDW=S027(U+(U+*(-1.25))/(R**4)-W**(-1.25)/(R**3)
          CDA=SGRT(W+(W**(0.25))*DDW)
          S=SQRT(EIK)
          XK=SQRT((S**2)*(R**2)+2*R-C)
IF(LP•EQ•0) GO TO 10
CTA=((C+0•125)/SQRT(C))*ACOS((R-C+S*C*XK)/((1•+(S**2)*C)*R))
GO TO 20 '
          CTA=1.7(4.+(XK+S+R))
        CTA=1./(4.*(XK+S+R))

ARG=XK+ALOG(1.+(S**2)*R+S*XK)/S+ARGM(EIK,LP)-1./S-ALOG(S)/S

$-3.1415926535*LP/2.+CTA-(XK*(3.*(S**2)*C+4.)*S*R*(3*S**2+2.)+S*C

$)/(24.*(1.+(S**2)*C)*XK*(XK+S*R))

$+5.*(R-C)/(24.*XK**3)

FI(I)=1./SQRT(CDA)*SIN(ARG)

IF(LP-J.) 4.5.4

B=EXP(-10.*R/(LP**2+LP))

COTO
  4
          GO TO S
    5
          B=0.
  5
          HI(I)=(1.-B)**(2*LP+1)*(1./SQRT(CDA))*COS(ARG)
          R=R+0.2
        DF=1./120*(6.*FI(1)-60.*FI(2)-40.*FI(3)+120.*FI(4)-30.*FI(5)
$+4.*FI(6))
12
          DH=1•/120•*(6•*HI(1)-60•*HI(2)-40•*HI(3)+120•*HI(4)-30•*HI(5)
        $+4.*HI(6))
F=FI(3)
H=HI(3)
          RETURN
          EÑÓ
```

FUNCTION ARGM(EIK+LP)
PI=2.
T=SCRT(EIK)
T=SORT(T)
SUB=(PI\*\*2)+(1./EIK)-(35./SORT(T1))
IF(SUE-0.6) 20.40.40
C PI=PI+1.0
G T 0 4
PI=PI+1.0
J=2
C 0 200 I=J.IN
S=ATAN(1./(I+T))
ARG=ARG=5
C C ONTINUE
ARGM=ARG-1./(2.\*T)\*ALOG(PI\*\*2+(1./(T\*\*2))-(PI-0.5)\*ATAN(1./(PI
\*T))+1./T+1./(12.\*T\*(1./T\*\*2+PI\*\*2))-(3.\*PI\*\*2-(1./T\*\*2))/
\$(360.\*(PI\*\*2+(1./T\*\*2))\*3)+(5.\*PI\*\*4-10.\*(PI\*\*2))/
\$(360.\*(PI\*\*2+(1./T\*\*2))\*3)+(5.\*PI\*\*4-10.\*(PI\*\*2))/
\$(1./T\*\*4))/(1250.\*T(PI\*\*2+(1./T\*\*2))\*\*5)
IF(LP=EG.0) GO TO 5C
ARGM=ARGM+ATAN(-1./T)
C C ONTINUE
RETURN
END

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C

C	SUBROUTINE FDIF(F.DF.FYI.FFYI) CONTINUUM WAVEFUNCTION COMMON X(10),EP(10).LP.EIK DIMENSION Y(2),C(24).W(2.9).FYI(22).FFYI(20).DFYI(22).FI(10). SFFFYI(30) DIMENSION FE(30) EXTERNAL REIR N=2 NW=2 TOL=1.0E-6 IND=1 R=22.
15	Y(1)=F Y(2)=DF FYI(22)=F DFYI(22)=CF D0 10 I=1.21 REND=22I CALL DVERK(N.REIR.R.Y.REND.TOL.IND.C.NW,W,IER) J=22-I FYI(J)=Y(1) DFYI(J)=Y(2) CONTINUE HELTE(6-100) (FYI(J)-1=1.22)
100 52	FORMAT(5x, "FYI=",/(2x, E10.4)) WRITE(5,52) (D=YI(I), I=1,22) FORMAT(5x, "DFYI=",/(5x, E12.4)) Y(1)=FYI(1) Y(2)=DFYI(1) DO 23 I=1.19 REND=10.05+I CALL DVFRK(N.REIR.R.Y.REND.TOLIND.C.NH.H.JFR)
23 309	FFYI(I)=Y(1) CONTINUE WRITE(5,300) (=FYI(I),I=1,19) FORMAT(5X,"FFYI=",/(5X,E12.4)) RETURN END

•

SUBPOUTINE PEIR(N+R+Y+YPRIME) COMMON X(10)+EP(10)+LP+EIK DIMENSION Y(N)+YPRIME(N) YPRIME(2)=(LP+(LP+1)/(R++2)-2+/R-EIK)+Y(1) YPRIME(1)=Y(2) RETURN END

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• • • SUBROUTINE HDIF(H.DH.HYI,HHYI) CONTINUUM WAVEFUNCTION С COMMON X(10),EP(10),LP,EIK DIMENSION Y(2),C(24),W(2,9),HYI(22),HHYI(25),DHYI(22),HI(10) EXTERNAL REIR N=2 NW=2 TŐL=1.0E-6 IND=1 R=22. Y(1)=H Y(2)=DH HYI(22)=H DHY1(22)=DH D0 10 I=1.21 REND=22.-I CALL DVERK(N,REIR,R,Y,REND,TOL,IND,C,NW,W,IER) J = 22 - IIF(LP.EG.0) GO TO 6 B=EXP(-10.\*R/(LP\*(LP+1.))) GO TO 5 B=0. 5 HYI(J)=Y(1) DHYI(J)=Y(2) CONTINUE WRITE(5,100) (HYI(J),J=1,22) FORMAT(5x, "HYI=",/(5x,E12.4)) WRITE(6,52) (DHYI(I),I=1,22) FORMAT(5x, "DHYI=",/(5x,E12.4)) Y(1)=HYI(1) Y(2)=DHYI(1) D0 23 J=1.19 10 100 52 DO 23 I=1.19 REND=1.-J.05\*I CALL DVERK(N.REIR.R.Y.REND.TOL.IND.C.NW.W.IER) HHYI(I)=Y(1)\*(1.-B)\*\*(2\*LP+1) CONTINUE 23 WRITE(5.300) (HHYI(I).I=1.19) FORMAT(5X,"HHYI=",/(5X,E12.4)) , 302 RETURN END

	FUNCTION FNLAF(X) DIMENSION PHMUT(30),PH(30)
	COMMON V(10)+EP(10)+LP+EIK+VIM+FYI(22)+HYI(22)+XX+FFYI(20)+
	\$HHYI(22)
	DU INU JEI022 DUNITAINEN
4	PH(J) = (x - I)/(J - I)
	PHMUT(J)=PHMUT(J)★PH(J)
100	CONTINUE
200	PHSUM=PHSUM+HIL(J)+PHMUI(J)
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300	ČŎŊŤĬŊĴĔ
•••	0089J=1.19
	PHMUT(J)=1.
	$D_{0}$ 80 $I = 1 \cdot 19$
4.0	
40	PH(J)=(X-0,05+1)/(0.05+(I-J))
<b>e</b> r	CONTINUE
0'2	
	PHSUM=PHSUM+HHYI(J)★PHMUT(J)
50	CONTINUE
422	IF(LP-0) 10,5,10
10	B==XP(-10+X/(_P++2+LP))
	AP=(1.++L1K*(LP*+2))*(1.++L1K)
5	
5	
6	HTOR=SQRT(3.1416/(2.+AP))
	CALL PBOUND(X,P)
	FNLAH=1•/(VIM**2)*((1•-B)**(2•*LP+1•))*P*X*PHSUM
	RETURN
	END

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SUBROUTINE PBOUND(R.P) BOUND RADIAL WAVEFUNCTION COMMON V(10).EI(10).L.EIK.VIM.FYI(22).HYI(22).XX CALL DEFECT(XX) CT=1.+2./VIM\*\*3\*DEFECT(YX) CALL MGAMMA(VIM+1.Y.IER) CALL MGAMMA(VIM+1.Y.IER) CALL MGAMMA(VIM.2.IER) PK=SGRT(CT\*(VIM\*\*2)\*Y\*Z) CALL SJMB(R.VIM) F=1./PK\*((2.\*R/VIM)\*\*VIM)\*(EXP(-R/VIM))\*SUMB(R.VIM) RETURN END

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FUNCTION SUMB(R.V) DIMENSION B(50).BB(50.50) INTEGER P P=1 IF(P-V) 2+2+3 P=P+1 2 IF(P-V) 2,2,5 P=P-1 IF(F-V) 4+2+3 P=P+1 3 4 5 B(1)=1. SUM=0. JK=P UN=F DO 10 K=1+JK B(K+1)=(V/(2+\*())\*(-(V-K)\*(V-K+1+))\*B(K) SUM=SUM+B(K)\*(3\*\*(-K+1)) SUM=SUM+B(K)\*((\*\*(-K+1)) CONTINUE KI=P+1 LI=P+9 DO 20 I=KI+LI B(I+1)=(V/(2.\*I))\*(-(V-I)\*(V-I+1.))\*B(I) BB(I+1)=B(I)\*((\*\*(-I+1))) CONTINUE LK=L 10 20 LK=LI-1 DO 30 J=1,5 LK=LK-1 DO 30 I=KI.LK BB(I.J+1)=BB(I+1,J)-BB(I,J) CONTINUE DIVE 30 CONTINUE DIV=0. DO 60 J=1.5 S=BB(KI.J)/(2.\*\*J) DIV=DIV+S CONTINUE SUME=DIV+SUM RETURN END 60 .

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	FUNCTION FNLAF(X) DIMENSION PFMUT(30)+PF(30)
	COMMON VIIUJEPVIIUJEPPEIKEVIMEPTI(22JEHTI(22JEXXEFFTI(2U)E
	PFYUT(J)=1-
	$DO 50 I = 1 \cdot 22$
	ÎF(I-J) 6,5C,6
6	PF(J) = (X - I) / (J - I)
	PFNUT(J)=PFNUT(J)+PF(J)
50	
	DU 50 0-1922 DESUM-DESUM-EVT(.1)+DEMUT(.1)
6.2	CONTINUE
	GO TO 4 DO
300	ĊŎŇŤĪŇŮĚ
	00 80 J=1+10
	PENUT(J)=1.
	00 80 I = 1 0 0
h C	1F(1-J) 4048040 DE(1)-1/4-0 0541)//0 054/7-1))
	PF(0)=(A=0.000=1)/(0.000=(1=0)/ PFNHT(1)=PFNHT(1)+PF(1)
80	
U	
	DO 100 J = 1 + 10
	PFSUM=PFSUM+FFYI(J)*PFMUT(J)
100	CONTINUE
<b>4</b> 0 C	IF(LP+IG+O) 60 TO 10
	AP=(1.+EIK+(LP++2))+(1.+EIK)
1 0	
20	FT0F=S0RT(3,1416+AP/2,)
20	
	FNLAF=1./(VIM**2)*P*X*PFSUM
	RETURN -
	END

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FUNCTION WKBF(X) COMMON XH(19), EP(10), LP+EIK, VIM C=LP+(LP+1.) W=EIK-C/X++2+2./X DW=2.+C/X++3-2./X++2 DDW=0.625+C+(W++(-2.25))+DW/(X++3)-0.625+(W++(-2.25))+DW/(X++2) \$+1.5+C+(W++(-1.25))/(X++4)-W++(-1.25)/(X++3) DDW=0.025+(W++(-1.25))/(X++4)-W++(-1.25)/(X++3) CDA=SQRT(W+(W\*+(0.25))+DDW)S=SQRT(EIK) XK=SGRT((S\*\*2)\*(X\*\*2)+2\*X-C) IF(LP.EQ.0) GO TO 13 CTA=((C+0.125)/SGRT(C))\*ACOS((X-C+S\*C\*XK)/((1.\*(S\*\*2)\*C)\*X)) GO TO 20 CTA=1./(4.\*(XK+S\*X)) ARS=XK+ALOG(1.\*(S\*\*2)\*X+S\*XK)/S+ARGM(EIK+LP)-1./S-ALOG(S)/S \$-3.1415926535\*LP/2.\*CTA-(XK\*(3.\*(S\*\*2)\*C+4.)+S\*X\*(3\*S\*\*2+2.)+S\*C 10 RETURN END FUNCTION WEBHER) COMMON XH(10) . EP(10) . LP . EIK . VIM C=LP\*(LP+1.)W=EIK-C/X\*\*2+2•/X DW=2•\*C/X\*\*3-2•/X\*\*2 DDW=0•625\*C\*(W\*\*(-2•25))\*DW/(X\*\*3)-0•625\*(W\*\*(-2•25))\*DW/(X\*\*2) \$+1•5\*C\*(W\*\*(-1•25))/(X\*\*4)-W\*\*(-1•25)/(X\*\*3) CDA=SGRT(W+(W\*\*(0.25))\*DDW) S=SQRT(EIK) XK=SQRT((S\*+2)+(X++2)+2+X-C) IF(LP.EG.0) GO TO 10 CTA=((C+0.125)/SQRT(C))+ACOS((X-C+S+C+XK)/((1.+(S\*+2)+C)+X)) GO TO 20 CTA=1./(4.\*(XK+S\*X)) ARG=\K+ALOG(1.+(S++2)+X+S+XK)/S+ARGM(EIK,LP)-1./S-ALOG(S)/S \$-3.1415926535\*LP/2.+CTA-(XK\*(3.\*(S\*\*2)\*C+4.)+S\*X\*(3\*S\*\*2+2.)+S\*C \$)/(24.\*(1.+(S\*\*2)\*C)\*XK\*(XK+S\*X)) \$+5.\*(X-C)/(24.\*XK\*\*3) •. IF(LP-0) 4.5.4 Ē=ĒXP(-10 .★X/(LP\*\*2+LP)) GO\_TO\_5 4 B=0. WKBHL=(1.-B)\*\*(2\*LP+1)\*(1./SQRT(CDA))\*COS(ARG) CALL PBOUND(X.P) WKBH=1./(VIM\*+2)\*P\*X\*WKEHL RETURN END

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FUNCTION DEFECT(X)
DIMENSION A(4),B(4),C(4),DP(4),XJ(4),U(4)
XJ(1)=-0.227
XJ(2)=-0.106
XJ(3)=-0.063
XJ(4)=-0.043
U(1)=0.90
U(2)=0.93
U(3)=1.02
U(4)=1.18
DO 33 J=1,4
A(J)=0.
DO 44 I=1,4
IF(I-J) 11,44.11
11 B(J)=(X-XJ(I))/(XJ(J)-XJ(I))
A(J)=A(J)*B(J)
C(J)=C(J)+1./(X-XJ(I))
44 CONTINUE
DP(J)=A(J)*C(J)
33 CONTINUE
DEFECT=0.
DO 55 J=1.4
DEFECT=0.FECT+J(J)*DP(J)
55 CONTINUE
RETURN
END
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FUNCTION DEFECT(X)
DIMENSION A(4),B(4),C(4),DP(4),XJ(4),U(4)
XJ(1)==0.227
XJ(2)==0.106
XJ(3)==0.063
XJ(4)==0.043
U(1)=0.90
U(2)=0.93
U(3)=1.02
U(4)=1.18
DO 33 J=1.4
A(J)=1.
C(J)=0.
DO 44 I=1.4
IF(I-J) 11,44.11
11 B(J)=(X-XJ(I))/(XJ(J)-XJ(I))
A(J)=A(J)+B(J)
C(J)=C(J)+1./(X-XJ(I))
44 CONTINUE
DEFECT=0.
DO 55 J=1.4
DEFECT=0.
DEFECT=0.FECT+J(J)+DP(J)
55 CONTINUE
RETURN
END
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