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Laser Optogalvanic and Photoacoustic Studies of Some Atoms and Small Molecules.

Phillip Lamar Clancy

*Louisiana State University and Agricultural & Mechanical College*

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LASER OPTOGALVANIC AND PHOTOACOUSTIC STUDIES OF SOME ATOMS AND SMALL MOLECULES

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LASER OPTOGALVANIC AND PHOTOACOUSTIC STUDIES OF
SOME ATOMS AND SMALL MOLECULES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Phillip L. Clancy

B.S., Louisiana State University, 1974
M.S., Louisiana State University, 1978
December 1986
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ABSTRACT

A device designed to perform laser optogalvanic (LOG) measurements on low pressure gases in an electrical discharge has been constructed. The device employs the unique combination of pulsed laser radiation in the visible range, and transverse excitation of a radiofrequency (RF) discharge to obtain high quality spectroscopic data on highly excited atomic and molecular species existing in an electrical discharge. The results of LOG studies on xenon, cesium, and nitrogen are reported.

In addition to functioning as a sensitive LOG detector, it has been discovered that the RFLOG device serves admirably as a contactless transducer of the photoacoustic signal. When the laser beam is focused into a region of the discharge cell some distance below the area of the discharge, excitation of ground state species gives rise to an acoustic wave through the photoacoustic effect. The acoustic wave causes a perturbation of the RF discharge which is detected by the RFLOG device. Results of a study on magnetic field induced level crossings in molecular iodine using photoacoustic detection with the RFLOG device are presented.

Finally, pulsed excitation has made possible time resolved studies of the response of the RF discharge to laser excitation. In studies on molecular iodine, it has been observed that subsequent to each laser pulse, two distinct signals are obtained. A fast signal, corresponding to absorption by iodine atoms occurs immediately upon pulsed excitation. A slower signal corresponding to absorption by molecular iodine follows some 200μs later. The results are
presented, and discussed in terms of the mechanism of the optogalvanic effect in atomic and molecular systems.
CHAPTER I
INTRODUCTION

1. Laser Optogalvanic (LOG) Spectroscopy*

The photophysics of highly excited states (i.e., electronic states 5000-100,000 cm\(^{-1}\) above the ground state) has received much attention in recent years. Various methods have been developed to study these high energy states. One such method is laser optogalvanic (LOG) spectroscopy.

The laser optogalvanic (LOG) effect represents the change produced in the electrical properties of a gaseous discharge when the discharge is illuminated with light of a wavelength corresponding to an electronic, rotational or vibrational transition (or any combination thereof) of some species in the discharge. Although the LOG effect has been known for over 50 years [1], it is only recently, with the advent of high-power, tunable lasers, that the technique has attracted much attention. Green and co-workers, in 1976, led this resurgence of interest in their study of the LOG effect in hollow cathode lamps, in which they demonstrated the very high sensitivity of LOG signals [2]. Since that time, many new electronic transitions in atoms [3,4,5,6] and molecules [7,8,9,10] have been observed using various modifications of the LOG technique.

*The terms "optogalvanic" and "photogalvanic" are used interchangeably in the literature, as are "optoacoustic" and "photoacoustic". The most common terms in general usage seem to be optogalvanic and photoacoustic. This latter convention will be adhered to in the present work.
In addition, transient radical species such as NH$_2$ [11] and HCO [12] were first studied at the Doppler limit using a variation of radiofrequency (RF) LOG spectroscopy. Lawler, et al. [13] developed a two-photon technique which has been used to achieve sub-Doppler measurements. This dual beam intermodulated technique was employed by Suzuki and Kakimoto [8], in conjunction with a ring dye laser, to obtain sub-Doppler measurements of N$_2$ Rydberg states. These experiments provide testimony to the high sensitivity and spectroscopic utility of LOG detection.

2. **Kinetics of the LOG Effect**

Efforts have been made to model the optogalvanic effect in a DC discharge [5,14,15,16]. These efforts are based on rate equations for processes occurring within the discharge. In the present Section, the mechanism of the LOG effect will be described in terms of gas discharge kinetics.

The species in the discharge are exposed to a high temperature and energetic free electrons. Sufficient amounts of energy are available to insure the population of states which are highly energetic in comparison to the ground state of a given species. Each of these states is characterized by a unique ionization rate which is a composite of the following four processes [17]. Electron impact ionization occurs from the ground state, as well as excited states. Associative ionization, which involves collision between an excited state of a given species and a ground state entity of the same species, results in the release of a free electron and consequent production of a molecular ion. Chemi-ionization occurs
only if the discharge contains more than one type of gas molecule. This involves an ionizing collision between a ground state molecule of one substance and an excited molecule of a second, different substance. Finally, collision between two long-lived, excited (metastable) molecules of the same substance can effect the release of a free electron and production of a molecular ion, and contributes strongly to the overall ionization rate. As many as 0.1% [17] of all molecular species in the discharge may be in an excited metastable state at any given time. It is reasonable that these states should be supposed to be the dominant species in sustaining a stable discharge.

Efforts to model discharge dynamics are based on iterative solutions of the complicated rate equations describing all of these ionization processes. These efforts, however, are hindered by a lack of knowledge of the cross sections for the various events and, as a result, progress is slow and limited to simple systems such as He [13,18] and other noble gases [16] in the positive column of a DC discharge.

The optogalvanic effect occurs when a laser beam influences the steady-state population existing in a stable discharge. The energy supplied by the laser may populate higher energy states at the expense of lower energy states, as in the case of absorption, or the exact reverse, as in the case of stimulated emission. The net effect, of course, will depend upon the detailed ionization kinetics of the states involved. If the laser populates a state with a high probability of ionization at the expense of a state with low
probability of ionization, the discharge voltage will decrease and
the discharge current will increase. If, on the other hand, the
laser populates an excited state possessing a high radiative
probability to the ground state, at the expense of a long-lived
metastable with a relatively high probability of ionization, the
discharge voltage will increase and the discharge current will
decrease. Thus, the sign of the optogalvanic signal in a DC
discharge may be either positive or negative.

3. Experimental Designs

Various experimental arrangements have been employed to
investigate the optogalvanic effect. Moreover, the various devices
have been used to obtain quantitative kinetic information as well as
spectroscopic data. Keller, et al. [5] have observed the $^{235}\text{U}/^{238}\text{U}$
isotope splitting by monitoring the current across a resistor in
series with a uranium hollow cathode lamp as the lamp was probed
with a tunable dye laser. The uranium, sputtered into the discharge
by electron bombardment during the course of normal lamp operation,
was centrally involved in the discharge dynamics.

Turk, et al. [19] constructed an apparatus to perform trace
analysis of substances in solution using the LOG effect (see Fig.
1). A pulsed laser was directed at the flame of a slot burner and
the material to be studied was aspirated into the flame. A tungsten
welding rod was situated on each side of the flame and a 1 kV DC
potential was applied between the rods and the burner head, with the
latter being connected to ground. Changes in current were monitored
FIGURE 1. Experimental apparatus used by Turk, et al. to obtain quantitative measurements using LOG detection.
Pulsed Laser \rightarrow \text{Burner Mixer} \rightarrow \text{Current Amp} \rightarrow \text{Gated Detection System} \rightarrow \text{Signal}

- \text{HV (d.c.)}
- \text{R}
- \text{10}^3 \text{ M Sample}
as the laser was fired into the flame and the signal was collected by a box car averager. Detection of 18 elements was reported, with the lower limits being 0.001-100 ng cm\(^{-3}\).

A typical arrangement for performing spectroscopic measurements on low pressure gases using LOG detection is presented in Fig. 2. In this set-up, two hollow electrodes are mounted within a pyrex discharge cell and the gas to be studied is made to flow at low pressure through the cell. A DC voltage of about 500 V is applied to the electrodes. A cw dye laser, which is chopped at the frequency \(f_R\), is directed through quartz windows and traverses the discharge. Changes in the discharge voltage occur as the laser is tuned through resonant frequencies and these changes are monitored by a lock-in amplifier operating at the chopping frequency. A series capacitor protects the lock-in amplifier from the high voltage of the discharge.

A significant improvement over the conventional, DC-discharge experiment is shown in the design of Fig. 3 [20]. In this arrangement, an applied RF field is used to create the discharge. Laser-induced impedance changes are detected either in the driving circuit [21-23] or by a separate antenna [20]. The primary advantage of this technique is that no internal electrodes contact the gas under study; thus corrosive gases can be investigated and the problem of reaction with the metal electrodes is avoided. A second advantage is that RF discharges can be sustained at lower pressures than can DC discharges. This permits application of sub-Doppler techniques [8] to molecular species. Lower pressures
FIGURE 2. A typical experimental design using a cw laser, DC discharge and LOG detection.
FIGURE 3. A typical experimental design using a radiofrequency discharge, cw laser and LOG detection.
also permit an increase in the population of high-energy species because of the lower probability of collisional depopulation.

The experiments to be described in this dissertation were performed with a device, shown in Fig. 4, which is a modification of that depicted in Fig. 3. The experimental details will be presented in Chapter II. Briefly, the differences between our device (Figure 4) and other radiofrequency LOG (RFLOG) designs (e.g., Fig. 3) are as follows: first, the continuous wave laser used by previous investigators has been replaced by a pulsed dye laser; and, transverse excitation rather than axial excitation was used in all experiments. This configuration represents the first combination of a pulsed dye laser and a radiofrequency discharge to perform LOG investigations.

The experimental results obtained using RFLOG detection and transverse excitation differ from the results of experiments employing DC discharge. Unlike the DC counterpart, the signal obtained with our device does not change sign, for a given laser power, as the laser is scanned: It is always positive or always negative. The sign of the effect does sometimes change, however, with changing laser power. Obviously, models developed to describe the DC LOG effect using axial excitation of the positive column are inadequate to describe RFLOG using transverse excitation.

Equipped with the device shown in Fig. 4, we set about performing spectroscopic investigations. We first turned our attention to xenon, a noble gas with closed shell configuration 5s²5p⁶. A study concentrating on pressure effects, field ionization
FIGURE 4. Experimental design employed in the present work using a radiofrequency discharge, pulsed laser, and transverse excitation.
LOG SET-UP WITH RF DISCHARGE

RF OSC.
-32 MHz

POWER AMP

SIGNAL RECOVERY

TO BOX-CAR

AMP

LASER
of high rydberg series and "λ-mixing" is presented in Chapter III.

A series of LOG experiments was also performed on Cs, an alkali metal of configuration 5s\(^2\)5p\(^6\)6s. Since Cs has a low vapor pressure at room temperature, it was necessary to heat the discharge tube in a make-shift oven. These experiments will be described in Chapter IV.

A third set of LOG experiments, those on molecular nitrogen (N\(_2\)), will be presented in Chapter V. We observed that only in a system with the gas flowing through the discharge tube could wavelength-dependent signals be obtained. Extensive data on the "First Positive System" of N\(_2\) will be presented.

4. The RFLOG Device Used As A Sonic Sensor

In addition to serving as a sensitive LOG signal collection system, we have discovered that our device functions admirably as a sonic transducer. It is known that the observed LOG signal is a function of the locus of laser excitation. This phenomenon has been studied using pulsed laser excitation by Haner, et al. [24] and by Rettner, et al. [25] in a DC discharge in pure I\(_2\). They observed a strong LOG signal (change in DC voltage) even when the laser beam was directed at a region of the discharge cell as much as 40 cm outside the discharge region [25]. Haner, et al. concluded that the laser beam initiated a pressure pulse which traveled down the tube and caused a mechanical perturbation in the discharge. This pressure pulse was supposedly produced by the degradation of electronic and vibrational energy to translational energy (E-T and
V-T transfer), and by dissociation of I₂ to I atoms. Time-resolved studies indicated that the pulse traveled at 100±20 m s⁻¹ which is, within experimental error, the velocity of sound in iodine at 250°C (110 m s⁻¹). Although they did not say so explicitly, Haner, et al. had observed the photoacoustic signal as a change in DC voltage. They did not, however, vary the wavelength of laser excitation and hence failed to record frequency-resolved spectra.

We have used this phenomenon to advantage in recording photoacoustic (PA) spectra with our RFLOG device. The technique, which we have dubbed PARFLOG, involves excitation of the discharge tube at a distance of several centimeters from the discharge region (i.e., in a region where the temperature of the gas approaches ambient temperature). Spectra recorded in this manner appear very similar to spectra recorded with a microphone and a conventional PA cell. That is, the discharge and signal pick-up system function as a contactless sonic transducer.

Conventional PA methods [26] for the study of gases employ microphones to monitor the PA signal. These methods suffer from three major shortcomings. First, a pressure sufficient to cause displacement of the diaphragm of the microphone must exist within the PA cell. For this reason, microphones cease to function at low pressures. Second, microphones cannot withstand studies at high temperature. Third, microphones are not suitable for studies of corrosive gases. Other contactless techniques have been developed [27,28,29,30], but none of these is superior to the PARFLOG technique, particularly with respect to low pressure sensitivity.
Results of PARFLOG experiments on magnetic field induced level crossings in I$_2$ will be presented in Chapter VI.

5. **Time-Resolved RFLOG Spectroscopy**

In experiments performed on I$_2$ vapors, we have observed two optogalvanic signals following each laser pulse. The first (fast) signal begins within the lifetime of the laser pulse and lasts only about 2 μs after termination of the pulse. The second (slow) signal begins about 200 μs after the laser pulse and lasts about 100-200 μs. Spectra recorded by monitoring the fast signal are identified here as resulting from absorption by dissociated I atoms. Spectra obtained by recording the slow signal reveal that it arises from absorption by I$_2$ molecules and corresponds to the PARFLOG signal. Thus, by selectively recording either the fast or slow signal, we are able to obtain information on I atoms or I$_2$ molecules under identical conditions of excitation. These data, along with a discussion of the implications of the time-resolved nature of the optogalvanic signal for the mechanisms of the optogalvanic effect, will be presented in Chapter VII.

6. **Organizational Note**

The organization of this dissertation is as follows:

--- Chapter I is intended to serve as a general introduction to LOG spectroscopy and to the technique of RFLOG in particular.

--- Chapter II is a general description of the experimental apparatus and methodology which is common to all of the experiments
presented in Chapters III-VII.

--- Chapters III-VII deal with individual experiments, including a description of the relevant experimental details. The basic results of the present work are presented in these chapters.
EXPERIMENTAL DETAILS

The apparatus used to perform PA and LOG experiments was home-made (cf. Fig. 4). The gas sample under study is contained in, or is pumped through, an 8 mm diameter quartz discharge cell. Two external electrodes are wound around the discharge cell and positioned a few centimeters apart. An RF generator (Wavetek Model 3000 signal generator) and amplifier (ENI model 320L) are used to supply as much as 20W of RF (32 MHz) power to a home-built resonant step-up transformer (turn ratio 20:1), which converts the potential into several thousand volts. This voltage, when applied to the external electrodes, is sufficient to initiate a discharge in a gas sample at low (30-1000 mtorr) pressure. RF power of 1-2 watts is generally sufficient to sustain a stable, low noise discharge.

The light source described by Kumar, et al. [31,32] was used as a source of pulsed, tunable laser radiation. This source is constructed around a Chromatix CMX4 flash-lamp pumped dye laser, the radiation output of which lies in the 720-435 nm region in the fundamental mode, and in the 365-265 nm region in the second harmonic mode. The bandwidth is ~ 3 cm\(^{-1}\) in the low-resolution mode and 0.1-0.2 cm\(^{-1}\) in the high-resolution mode, which uses an intracavity etalon. The laser is capable of producing several mJ of energy (several kW power) in pulses of about 1 µs duration. The laser was operated routinely at a pulse repetition rate of 6-10 pps.

Signal recovery is accomplished by means of a pick-up coil wound around the discharge cell and positioned 8-10 mm below the
lower RF electrode (see Fig. 5). This resonantly-tuned pick-up coil is inductively coupled to the discharge and functions as a receiving antenna, which is sensitive to any change in the impedance of the discharge. The pick-up coil is connected to a home built diode bridge circuit which functions as a full-wave rectifier. The signal is read as a change in DC output of the diode bridge, and appears as a transient pulse when the rectifier output is displayed versus time on an oscilloscope. The gate of a boxcar integrator (PAR Model 160) is set to monitor the pulse on the oscilloscope. Signal normalization for pulse-to-pulse variations in laser power is accomplished as described by Kumar, et al. [31,32]. The normalized signal is recorded versus wavenumber as the laser is scanned. An autoscanner (Chromatix CMX4/ASA) controls the scanning of the laser and the operation of the two channel x-y recorder (Hewlett-Packard Model 7046A). Wavelength calibration markers are produced by directing a portion (5%) of the laser beam into a hollow cathode lamp and monitoring the current delivered to the lamp across a series resistor. Changes in lamp current due to the optogalvanic effect [33] are produced when the laser is scanned through an absorption frequency of the species in the lamp. These changes in lamp current are amplified and sent to the second channel of the x-y recorder.

As described in Chapter I, in a stable discharge there exists a dynamic equilibrium in which there is an appreciable population of high-energy metastable states. Conditions such as pressure, RF power, frequency and the nature of the species under study determine
FIGURE 5. Experimental configuration showing locus of laser excitation for: (a) RFLOG, and (b) PARFLOG.
the equilibrium population distribution. This steady state results in the transference of a constant amount of power to the pick-up coil. When the discharge is perturbed by some external influence, the amount of power transferred to the pick-up coil changes, which gives rise to a transient change in the DC output of the diode bridge circuit. This, in turn, produces the LOG or PA signal.

Two experimental configurations were used in the present work. In the first configuration, the laser beam is directed into the lower region of the RF discharge (i.e., the region between the pick-up coil and the lower RF electrode). When the laser is tuned through a frequency resonant with an electronic transition, a shift in the stable distribution of populated states results. The perturbed discharge condition is characterized by a different ionization threshold than that of the unperturbed condition, which results in a change in voltage-current characteristics of the plasma. This is sensed by the pick-up coil as a change in the power that is transferred to the pick-up coil, and provides the LOG signal.

In the second configuration, the laser beam impinges on the cell at a location several centimeters below the discharge region (see Fig. 5). This region of the cell is quite cool and it exhibits a population distribution that characterizes this lower temperature. Ground state molecules predominate and electronically excited species are so rare as to be undetectable. When the laser is tuned through a frequency resonant with an electronic excitation of the ground state, laser energy is absorbed. A portion of the absorbed
energy is released in non-radiative modes and gives rise to a sonic wave induced by the photoacoustic effect. The sonic wave propagates upward through the cell at the speed of sound under the existing conditions of temperature and pressure. Upon reaching the region of the discharge, the wave produces a mechanical perturbation of the discharge, which is sensed by the pick-up coil. The result is the detection of the PA signal as a transient change in power transferred to the pick-up coil. This power change is monitored as a change in the DC output of the diode bridge and constitutes the PA signal.

The term impedance spectroscopy [34] is best used to encompass both the LOG and PA experiments which comprise the present work. Although both techniques are performed using the same apparatus, the differences are fundamental and should be emphasized. The LOG technique is used to investigate high energy, transient species, such as radicals or metastables which exist within the plasma itself. The PARFLOG experiments provide information on ground state molecules. The spectra obtained in the latter case are similar to the PA spectra recorded with a microphone. However, the PA technique performed using impedance spectroscopy has the advantages that studies may be done at much lower pressures than with conventional methods and also that experiments can be performed on corrosive gases.
A. PREAMBLE

A good candidate for study by the RFLOG technique must meet certain criteria. First, the sample must possess sufficiently high vapor pressure to exist at least partially in the gas phase under the specified experimental conditions. Second, the gas must be non-reactive within an electrical discharge. A substance which fulfills these requirements admirably is atomic xenon (Xe).

Xenon is a noble gas of atomic number 54: It possesses the closed shell electronic configuration $5s^25p^6(^1S_0)$ and, hence, is, notoriously unreactive. In addition to low reactivity, xenon possesses a sufficiently low boiling point (166.1 K) to exist entirely in the gas phase at the pressures within the discharge cell (40-800 mTorr).

The coupling scheme which is conventionally used to describe the spectra of electronically excited xenon is the $(j,\ell)$ scheme in which electrostatic interactions are weak compared to the spin-orbit interactions of the core, but strong compared to the spin-orbit interaction of the optical electron. The total angular momentum $j$ of the parent ion (3/2 or 1/2) and the orbital angular momentum ($\ell$) of the external electron (0,1,2,3 for s,p,d,f, respectively) couple to form resultant $K$, which then couples with the electron spin ($\pm1/2$) to yield $J$. According to this scheme, level designations are $n\ell(K)J$ and $n\ell'(K)J$ for states built on the $^2P_{3/2}$ and $^2P_{1/2}$ configurations of the core, respectively. The optical selection
rules for dipole radiation are $\Delta j = 0; \Delta K = 0 \pm 1$ and also $\Delta j = 0, \pm 1, 0^{+}0$.

The spectra obtained in our RFLOG experiments on xenon, are less complicated than those obtained with some other atomic species. In the first place, the large spin-orbit splitting of the core (10,537 cm$^{-1}$) insures a minimum of channel interactions between the $\ell$ and $\ell'$ channels. Indeed, only six states of the n$^2\ell'$ series lie below 97,834.4 cm$^{-1}$, the value to which the n$^2\ell$ series converge. Second, in the spectra obtained with our apparatus, the isotope splitting is not resolved. Thus, atomic lines are not complicated by isotope splittings.

Spectra obtained by probing RF discharges in xenon were identified and assigned based on the tables of energy levels of C.E. Moore [35]. A computer program was written to generate all possible differences of term values, within the constraints of the selection rules for dipole radiation. It was discovered that series arising from the (5p$^5$)p and (5p$^5$)d states were abundant under our experimental conditions. Of these, the (5p$^5$)p states are known (the p states, of course, are optically accessible from the ground state 5s$^6$ configuration). The series arising from the (5p$^5$)d states, on the other hand, were not completely known. According to the ($j\ell$) coupling scheme there should exist eight levels of the (5p$^5$)d configuration (see Fig. 7, below). We have observed 5d+nf series arising from all eight of the 5d levels. Only four of these 5d-nf series had been previously reported. The new series reported here are the 5d(1/2)1+nf, 5d(3/2)2+nf, 5d(7/2)4+nf, and 5d(7/2)3+nf.

The observation of the new series, along with additional
results of our RFLOG experiments will be described in Section B of this chapter. Additional studies on pressure effects, magnetic field induced ionization and spectral broadening due to \( \ell \)-mixing will be presented in Section C of this chapter.

It is curious that the four new series arising from the 5d states had not been observed by other groups who studied xenon using the RFLOG technique. In particular, researchers at both the Laboratoire de Spectroscopie Hertzienne, Universite Pierre et Marie Curie [36] and the Laboratoire de Spectroscopie Atomique, Universite de Caen [37] used a high-resolution continuous wave laser to probe the spectral characteristics of an RF discharge in xenon. Both groups used laser excitation in the visible region and xenon pressures in the range 100-400 mTorr. In many respects, the experimental arrangements used by the French investigators were similar to those used by us; however, theirs differed from ours in two important respects. First, the source of laser power was a cw ring dye laser and, second, the laser output was directed axially (i.e., along the long axis of cylindrical discharge cell). Perhaps due to one or both of these factors, the spectra obtained by the French investigators were dominated by transitions arising from 5p levels, specifically 5p+ns and 5p+nd. The major achievement reported in the present Chapter is that, using our unique, pulsed variation of RFLOG spectroscopy and transverse excitation of a cylindrical discharge tube, we have conducted a thorough study of the 5d+nf series in XeI, including 4 series never before observed.
B. PULSED LASER OPTOGALVANIC SPECTROSCOPY OF
Xe IN AN RF DISCHARGE

1. Introduction

The advent of the tunable laser has revived the optogalvanic effect, first discovered by Penning [1] in 1928, as the basis for a new powerful, sensitive and simple spectroscopic technique. This technique is laser optogalvanic (LOG) spectroscopy: A laser beam incident on a plasma of highly excited species that may exist in a discharge, flame, etc. produces, when absorbed, a change of the existing equilibrium conditions. The shift of the equilibrium and/or the process (rate) of its restoration may be detected by devices as simple as a pick-up coil (in the case of a RF discharge), and produces the so-called optogalvanic signal. The parameter that is actually measured is the change of discharge impedance produced when a plasma constituent absorbs the output light of the tunable laser. Thus, the spectroscopic utility of the optogalvanic effect implies a laser wavelength dependence of the LOG signal.

The actual capability of the LOG method, which already has found application in atomic and molecular spectroscopy, in the frequency stabilization of gas lasers and in the study of exotic species in discharges and flames [38], remains to be explored. In particular, a great number of parameters seem to influence both the type of response and the nature of the signal. The main advantage of the LOG technique is its ability to extract signals from
low-pressure, radiative sources where absorption, laser optoacoustic or laser-induced fluorescence detection sensitivities are too low.

In this Section, we report the LOG spectra of xenon in a 32 MHz RF discharge obtained by using a flash-lamp pumped tunable dye laser in the wavelength region 16,200-16,800 cm$^{-1}$.

2. **Experimental**

Several aspects of the experiment are original. These are:

(i) since a pulsed laser was used, the signals had to be normalized \([31,32]\) before averaging on a pulse-by-pulse basis; (ii) the effective duty-cycle had to be forced \([31,32]\) toward unity in order to obtain smooth, high-resolution spectra even at low pulse-repetition rates; (iii) as a result of numerous trial and error attempts to optimize the parameters influencing the spectra, it was found that closed systems (quartz tubes of $\phi$ 5 mm) and xenon pressures between 40 to 100 mTorr were of greatest advantage; (iv) the RF supplied by the two externally-mounted copper electrodes, when brought into resonance with the discharge, required powers of only a few watts in order to sustain the discharge; and (v) excellent LOG signals were obtained when the pick-up coil was displaced relative to the RF electrodes and when a transverse optical excitation was imposed in the region between the pick-up coil and the RF electrode.

In contrast to the LOG signals obtained with cw axial excitation \([20,36,37,39,40]\) which produces both positive and negative
signals, the present technique yields positive signals only. The cell configuration, excitation and pick-up are shown in Figure 4. A higher gas pressure or signal pick-up in a different region of the cell produce large effects on the spectrum, changing both the relative and absolute intensities of various spectral lines.

3. Results and Discussion

A typical low-resolution ($\Delta \nu \approx 3\text{cm}^{-1}$) LOG spectrum of 100 mTorr xenon in a 32 MHz discharge ($\sim 1$ watt), obtained as described, is shown in Figure 6. As is indicated by the appended assignments, most lines correspond to transitions from states which derive from the $5p^5d$ configuration of neutral xenon (cf. Fig. 7). Xenon, with electronic configuration $np^6(1S_0)$ in the ground state, yields, under our RF excitation conditions, two configurations of the type $np^5nl$, one with a $^2P_{3/2}$ core ($n\ell$-states) and the other with $^2P_{1/2}$ core ($n\ell$-states). The notation used in Figure 7 is the $j\ell$ coupling scheme of Racah [41], namely $n\ell(K)J$. The five series which are seen originate in the $5d(1/2)0$, the $5d(1/2)1$, the $5d(3/2)2$, the $5d(7/2)4$ and the $5d(7/2)3$ states [35] at 78771.79, 79987.16, 80323.28, 80197.16 and 80970.93 cm$^{-1}$, respectively, and they terminate on $nf$-states (see Fig. 7). To our knowledge, despite much work on the higher excited states of xenon [42-48], and considerable recent work employing LOG spectroscopy [39], only one of these series has been reported previously. An increase of xenon pressure or signal pick-up interior to the discharge region (i.e., between the RF
FIGURE 6. Low-resolution LOG spectrum of xenon from 16,200 - 16,800 cm$^{-1}$. The lines corresponding to the transitions $5p^{5}d$-$nf$ states are labelled. The wavelength calibration markers generated from a hollow cathode lamp, with neon as filler gas, are displayed in the upper part of the spectrum.
FIGURE 7. Partial term diagram for xenon.
Xe I

\(108371.4 \text{ P}_{1/2}\)

\(97934.4 \text{ P}_{3/2}\)

\(\times 10^3/\text{cm}^{-1}\)

\(\text{ns}^*\) \hspace{1cm} \(\text{np}^*\) \hspace{1cm} \(\text{nd}^*\) \hspace{1cm} \(\text{nf}^*\)

\(10 \text{ s}^*\) \hspace{1cm} \(9 \text{ s}^*\) \hspace{1cm} \(7 \text{ d}^*\) \hspace{1cm} \(7 \text{ f}^*\)

\(9 \text{ s}^*\) \hspace{1cm} \(8 \text{ s}^*\) \hspace{1cm} \(6 \text{ d}^*\) \hspace{1cm} \(4 \text{ f}^*\)

\(7 \text{ s}^*\) \hspace{1cm} \(7 \text{ p}^*\) \hspace{1cm} \(6 \text{ p}^*\) \hspace{1cm} \(6 \text{ f}^*\)

\(6 \text{ s}^*\) \hspace{1cm} \(6 \text{ p}^*\) \hspace{1cm} \(5 \text{ d}^*\) \hspace{1cm} \(4 \text{ f}^*\)

\(6 \text{ s}^*\) \hspace{1cm} \(6 \text{ p}^*\) \hspace{1cm} \(6 \text{ s}^*\) \hspace{1cm} \(6 \text{ f}^*\)

\((5p^5)s\) \hspace{1cm} \((5p^5)p\) \hspace{1cm} \((5p^5)d\) \hspace{1cm} \((5p^5)f\) Configuration
electrodes) produces a dramatic increase in the intensity of those lines that originate in the \((5p^5)p\) configurations. We will confine ourselves mainly to the new \(f+d\) transitions and we will provide a brief discussion of the characteristics of these four series.

The 5d\((1/2)\)0+nf\((3/2)1\) Series: The two members which terminate on the 8f\((3/2)1\) and 9f\((3/2)1\) states and which occur at 16323.2 cm\(^{-1}\) and 16691.38 cm\(^{-1}\), respectively, are of low intensity in the LOC spectra (Fig. 6.) The nf\((3/2)1\) series is the most investigated series in xenon since it is most easily accessible from other states. The observed energies of 96097.0 and 96463.2 cm\(^{-1}\) are in good agreement with existing experiment.

The 5d\((1/2)1\)+nf Series: Only two members of this medium intensity series, both of which terminate on the 9f\((3/2)1,2\) and 10f\((3/2)1,2\) states, are shown in Fig. 6. They occur at 16484 cm\(^{-1}\) and 16738 cm\(^{-1}\), respectively. The latter state, as shown at high resolution (\(\Delta v \sim 0.1\) cm\(^{-1}\)) in Fig. 8, is actually a doublet with 0.5 cm\(^{-1}\) spacing, the \((3/2)2\) component being of somewhat higher intensity. These states, according to Moore [35], are degenerate and lie at 96725 cm\(^{-1}\). The present results indicate that the degeneracy is split, the two components lying at 96725.04 cm\(^{-1}\) and 96725.58 cm\(^{-1}\) for the 10f\((3/2)1\) and 10f\((3/2)2\) terminal states, respectively.

The 5d\((3/2)2\)+nf Series: Members with \(n = 10, 11\) and 12 are shown in Fig. 6. In high resolution (Fig. 8), the 12f member consists of two
FIGURE 8. High resolution LOG spectrum obtained in the region 16,720 - 16,750 cm$^{-1}$, with an appended assignment of the observed lines.
doublets, one at 16742.06 cm\(^{-1}\) and 16742.43 cm\(^{-1}\), and the other at 16745.00 cm\(^{-1}\) and 16745.29 cm\(^{-1}\) (shoulder). By extrapolation from lower energy nf states, these transitions correspond to excitation to a 12f(3/2)1 and 12f(3/2)2 doublet, and a 12f(5/2)3 and 12f(5/2)2 doublet, respectively. The most intense progression in this series is in the (5/2)3 component. With the exception of the 12f(3/2)1 excitation which was previously reported [39] as a member of the 6s'(1/2)0+n f(3/2)1 series, these states are reported here for the first time. The agreement for the 12f(3/2)1 state, namely 97065.1 cm\(^{-1}\) versus the present 97065.34 cm\(^{-1}\), is very good.

The 5d(7/2)4+nf Series: In this series, the members \(n = 9, 10,\) and 11 are of highest intensity (Fig. 6). At high resolution (Fig. 8), the 11f member consists of two unresolvable doublets, one at 16722.91 cm\(^{-1}\) corresponding to the 11f(9/2)5,4 states (96920.07 cm\(^{-1}\) vs. 96919.72 cm\(^{-1}\) in [35]) and a much weaker one at 16726.95 cm\(^{-1}\) corresponding to the 11f(7/2)4,3 states (96924.11 cm\(^{-1}\)) which had not been reported previously. The very weak peak at 16725.12 cm\(^{-1}\) is tentatively assigned to the 11f(5/2)3 terminal state of energy 96922.28 cm\(^{-1}\) in [35].

The 5d(7/2)3+nf Series: This is the most interesting series of those described in the present study (cf. Fig. 6). The members \(n = 14\) to 40 are observed. In accordance with results of Grandin and Husson [39], who observed a similarly long progression of the nf (3/2)1 series originating in the 6s'(1/2)0 level, we find that these
levels fit the Rydberg formula with a quantum defect value $\mu = 0.06$.

From high resolution measurements of the 20f and 21f series members, the presence of the $(9/2)4$ and $(7/2)3,4$ components is indicated. Additional measurements of the 8f member also suggest the presence of a very low intensity transition to the $(5/2)3$ state.

In proceeding to higher members of this series ($n>20$), an interesting feature, namely the deterioration of the band structure, is observed. In Fig. 9, where members 28-31 appear at 16723.0, 16732.3, 16741.1 and 16748.7 cm$^{-1}$ respectively, this deterioration is readily observed. The intensity, shape and overall appearance of these peaks ($n>20$) are dramatically altered by a variety of experimental parameters, rendering them stronger, broader or even causing their complete disappearance. The broad, asymmetrical shape indicates that these states are autoionized and, since their energy is below ionization threshold, the process presumably is promoted by field effect. This is hardly surprising: High Rydberg states are characterized by a polarizability that increases as $n^6$, and the applied RF field represents several hundred V/cm. As shown in other cases [35], conditions are ideal for field ionization. A typical recording (cf. Fig. 9) of the region 16700 - 16770 cm$^{-1}$, where members $n=26-40$ of this series appear, depicts this field ionization quite clearly. The spectra (a) and (b) in Fig. 9 refer to two different discharge conditions and were recorded at low resolution ($\Delta v \approx 3$ cm$^{-1}$). The loss of intensity and disappearance of the high $n$ states in Fig. 9(b) is attributed to the larger field strength present under the latter discharge conditions. Such effects,
FIGURE 9. Field-ionization effects on the higher members of the $5d(7/2)3+nf$ transition under medium resolution.
however, are not limited solely to this series. Other series originating from states of the \((5p^5)d\) configuration should exhibit a similar behavior.

In conclusion, even for simple atoms such as xenon, LOG spectroscopy makes possible the excitation of otherwise unattainable highly excited electronic states and the study of their properties.
C. OPTICAL TRANSITIONS IN HIGHLY EXCITED STATES: RFLOG SPECTRUM OF XeI

1. Introduction

Atomic spectroscopy [49] has provided the basic information and played the dominant role in the development and growth of quantum theory. The continuous interplay of experiment and theory has characterized this development and, even today, it continues to produce new insights into the behavior of electrons in atoms and molecules. In particular, the advent of the laser and its use in conjunction with discharges, particle beams and strong electric and magnetic fields has revolutionized the study of highly excited states. A plethora of new techniques has evolved, and certain results derived from them constitute a strong challenge even for atomic theory.

In this Section we present results for some highly excited states of xenon. These results were obtained by laser optogalvanic (LOG) spectroscopy of a 32 MHz radio-frequency (RF) discharge [38] in a diluted gas in a closed system. Pulsed dye laser excitation in the wavelength range 14000 - 17000 cm\(^{-1}\) was used. This work is a continuation of the RFLOG studies of xenon [6] described in the previous Section. The LOG method [38,42], in several modifications, is particularly suitable for the generation and study of highly excited states of atoms and molecules. In particular, the RF discharge [38] has the distinct advantage that the electrodes, being external, are not subject to attack by the gas under investigation.

Several studies of xenon using RFLOG variants have appeared recently [36,37,39,40,50]. Indeed, taken in conjunction with recent

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results on the properties of highly-excited states obtained by other methods [43,45,51], xenon has become an important test of theories and models for the interpretation of complex atomic spectra [44,46,48,52,54]. Indeed, spectra are now readily obtained in steady, pulsed or oscillatory electrical and magnetic fields, and the effects of collisions of highly excited, Rydberg states with inert and reactive gases or absorption of blackbody radiation by them are readily measured [55]. And, finally, the ready accessibility of atoms and molecules in exotic states which had previously been known only from astrophysical observations provides a strong impetus for intense study.

2. **Experimental**

Several aspects of our technique are original [6]: the use of a pulsed laser, the external supply of RF power and external signal pick-up. Since a pulsed laser was used, the signals had to be normalized on a pulse-by-pulse basis before averaging; and, since the pulse repetition rate was low, the effective duty-cycle had to be forced toward unity in order to obtain smooth high resolution spectra. Closed systems (quartz tubes of $5 \text{ mm}$) and xenon pressures between 0.04 and 1 Torr were found to be optimal for the maintenance of a stable discharge and for the study of pressure effects. The RF field, as supplied by two externally mounted copper electrodes, when brought into resonance with the discharge required powers of only a watt or so to sustain a stable discharge —— an important consideration because both the pressure and the discharge intensity may shift and broaden the spectral lines. Excellent LOG signals were obtained when the pick-up coil was displaced
relative to the RF electrodes, and when a transverse optical excitation was imposed in the region between the pick-up coil and the RF electrodes.

3. Results and Discussion

The topic of interest is the effect of gas pressure on the RF LOG spectra of xenon. In discussing these effects, one must keep in mind the electronic configuration of the xenon atom, as well as the characteristics of the technique that produces the LOG signals in the RF discharge.

In xenon, a rare gas with a closed valence shell configuration \( \ldots 5s^25p^6(^1S_0) \) in the ground state, the excitation of a \( p \) electron yields two \( 5p^5n\ell \) configurations one with a \( ^2P_{3/2} \) core (\( n\ell \)-states) and the other with a \( ^2P_{1/2} \) core (\( n\ell' \)-states). Thus, all levels of \( \text{XeI} \) in which we are interested may be considered as built on either the \( ^2P_{1/2} \) or \( ^2P_{3/2} \) state of the ionic core.

The experimental term scheme [35] of \( \text{XeI} \) is shown in Fig. 7. Because of the large splitting of the ionic core (~10,000 cm\(^{-1}\)), most \( n\ell' \) states are autoionizing levels located above the \( ^2P_{3/2} \) threshold to which the \( n\ell \) series converge. Those which lie below the \( ^2P_{3/2} \) threshold may be strongly perturbed by channel interactions: Thus, rare gas spectra often exhibit large shifts of energy and intensity because of interaction between levels of the same parity and \( J \) (e.g., \( np \) by \( np' \)). In xenon, however, only \( 6p' \), \( 5d' \) and none of the \( n\ell' \) levels lie below the \( ^2P_{3/2} \) limit and, therefore, these effects are small. Unfortunately, even the \( (j\ell) \)-coupling model is not entirely satisfactory.
forbidden transitions for which $\Delta j \neq 0$ are observed (e.g., $s'-p$, $s'-f$, $d-f'$); the intensities of nominally allowed transitions do not maximize when $\Delta K = \Delta J$; and transitions with $\Delta K = 2$ are frequently observed.

The RF LOG technique depends on the interplay of several events in order to yield a spectrum: the RF discharge creates a pseudo equilibrium set of excited states which depends sensitively on frequency, power, local temperature and pressure. In addition, the RF discharge may produce large variable electric and magnetic fields which (vide infra) have severe consequences for the fate of high series members. The discharge itself is probed by a tunable laser beam which, when absorbed, changes the equilibrium set. The shift in this equilibrium and/or the process (rate) of equilibrium restoration produces a change of discharge impedance which is detected by a pick-up coil, thus producing the so-called optogalvanic signal.

The recorded spectrum, then, depends on the density and lifetime of the absorbing states in the discharge, the transition probability to higher excited states and, particularly, on the impedance change that this process produces in the discharge. As a result, the LOG signals may be either positive or negative. Indeed, it is entirely possible that certain transitions will produce no signal at all, in which case the absence of a signal does not imply the absence of such transitions. Under our conditions, when the laser excitation occurs at the edge of the discharge, only positive signals are observed.

The low resolution ($\Delta \nu \approx 3 \text{cm}^{-1}$) RFLOG spectra of 40 and $\approx 950$ mTorr xenon in a 32 MHz discharge ($\approx 1 \text{ W}$), are shown in Figs. 10, 11 and 12. The regions 14000-15000 cm$^{-1}$, 15000-16000 cm$^{-1}$ and 16000-17000 cm$^{-1}$ are
FIGURE 10. Low resolution RFLOG spectrum of 40 mTorr (upper part) and 950 mTorr (lower part) xenon in a 32 MHz discharge recorded in the region 14,000-15,000 cm\(^{-1}\).
FIGURE 11. Low resolution RFLOG spectrum of 40 mTorr (upper part) and 950 mTorr (lower part) xenon in 32 MHz discharge recorded in the region 15,000-16,000 cm\(^{-1}\).
FIGURE 12. Low resolution RFLOG spectrum of 40 mTorr (upper part) and 950 mTorr (lower part) xenon in a 32 MHz discharge recorded in the region 16,000-17,000 cm$^{-1}$. 
shown in the upper (a) and lower (b) parts, respectively, of these figures. It is evident that higher pressures produce large alterations of the spectrum. For example, the intensities of the spectral lines change both relatively and absolutely.

As indicated in the figures, the low pressure spectra are dominated by seven composite series of 5d-nf transitions. An eighth series, which originates from the 5d(3/2)1 level, terminates below 14000 cm$^{-1}$ (see Table I) and was not subjected to much study*. Some of the 5d-nf series have been reported recently [6,37,50]. The newly reported series presented here are the 5d(5/2)2 + nf and 5d(5/2)3 + nf series, with limits at 15908 and 15403 cm$^{-1}$, respectively. The former consists of transitions to (5/2)2, (5/2)3, and (7/2)3 and the latter to (3/2)2, (5/2)2, (5/2)3, (7/2)3, (7/2)4, and (9/2)4 nf-levels. This last series, as well as the 5d(1/2)1 + nf(5/2)2 (Table I), violates the (j\ell)-selection rules.

*Footnote: We have been able to detect some members of this series in region above 13870 cm$^{-1}$ (i.e. close to its limit at 13944 cm$^{-1}$); but, because of the low laser power available to us in this region, no significant study of this series was attempted.
### TABLE I. Observed d-f transitions between 14000 and 17000 cm⁻¹

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<td>6-10</td>
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<td>5d[1/2]₁</td>
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<td>+</td>
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<td>5d[3/2]₂</td>
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<td>5d[5/2]₂</td>
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<td>+</td>
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<td>8-lim</td>
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<tr>
<td>5d[5/2]₃</td>
<td>+</td>
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<td>3-lim</td>
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<tr>
<td>5d[7/2]₃</td>
<td>+</td>
<td>+</td>
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<td>5d[7/2]₄</td>
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**Upper level nf**
The results of Table I were obtained at high resolution. That is, once the location of a composite series member was determined in the low resolution spectrum, its components, their intensities and exact positions were measured using an intracavity etalon of about 5 cm\(^{-1}\) free spectral range. These scans were always initiated at a calibration marker (neon hollow cathode lamp), with further calibration being performed by means of fringe counting to an accuracy of about 0.2 cm\(^{-1}\).

As an example, the highly resolved part of the RF LOG spectrum at 16730 cm\(^{-1}\), shown in Fig. 13, exhibits several d-f series members (i.e., 10f from 5d(1/2)1, 11f from 5d(7/2)4 12f from 5d(3/2)2 and 28f-31f from 5d(7/2)3) and one p-d transition (i.e., 6p(3/2)2 + 10d(5/2)3).

Once accurate energies of the observed lines are known, the energies of the higher nf-levels can be readily determined. In Fig. 14, these values are shown diagramatically for n=8 to 12 indicating that with increasing n the energy separations of the levels decrease rapidly. Indeed, at n=20, this K-span extrapolates to less than 2 cm\(^{-1}\), a fact that is of some help in explaining the behavior of the high series members which, as stated, collapse and disappear before reaching the ionization limit [39,40,44,50]. This gradual collapsing is evident in Fig. 13 for the n=29f-31f members of the 5d(7/2)3-nf series.

At which member the nf series disappears depends primarily on discharge conditions: The weaker the discharge the greater is the chance to observe those series members that lie close to the ionization limit. Since the disappearance of the bands is undoubtedly connected to an ionization process, it is reasonable to assume that field ionization is the culprit. That is, in the high-energy states for which n>30, the
FIGURE 13. High resolution RFLOG spectrum of 40 mTorr xenon around 16,370 cm$^{-1}$. 
The diagram shows a spectrum with various labeled transitions. The transitions are labeled with quantum numbers and energy levels, such as $11f(9/2)_2$, $11f(7/2)_2$, $10d(5/2)_3$, $10f(3/2)_1$, $12f(3/2)_2$, and $12f(5/2)_3$. The energy scale is labeled in cm$^{-1}$, ranging from 16730 to 16750. The transitions are indicated by arrows pointing between the levels. The diagram also includes a label for $Ne$. The transitions are marked with quantum numbers representing different angular momentum states.
FIGURE 14. Experimental state energies of xenon nf-states, n = 8-12.
energy provided by the RF field is adequate to produce field ionization. The other phenomenon, to which we have made reference as a "collapse" but which really is a massive broadening of the high-n members, is also intriguing. This behavior had been attributed to collisional effects. However, it is now becoming clear that this broadening is attributable to an λ-mixing that takes place in the upper state and that is caused by the presence of electric and magnetic fields in the RF discharge. Since the polarizability of Rydberg atoms [56] increases as n^6, it is clear that, for high n, relatively weak fields can produce considerable mixing. Two recordings of the 5d(1/2)3 + 29f peak are shown in Fig. 15 under stronger (a) and weaker (b) discharge conditions. It has been shown [37,50] that such xenon peaks split into complicated but interpretable patterns in a magnetic field of about 1-2 T; however, in that case it was necessary to use an isotopically enriched sample and a line originating from the 5d(1/2)0 which terminates only in nf(3/2)1 (cf. Table I) in order to resolve the pattern.

In conclusion, a few words on the pressure effect: The evident effect of increased pressure is that transitions from lower energy and lower angular momentum (e.g., s, p) levels become more important. This finding can be explained in two ways: either the existing low power of the discharge is inadequate to provide the requisite energy to the increased number of atoms that would permit attainment of higher energy levels, and/or the population of higher energy states is decreased by the greater probability of collisions. Also, our results seem to confirm previous findings that transitions into high p states are of lower intensity --- a fact previously attributed to the interaction of
FIGURE 15. Two recordings of the 5d(1/2)3→29f peak under stronger (a) and weaker (b) RF discharge conditions.
16730.27 cm$^{-1}$ (Ne)

$6p[3/2]_2 \rightarrow 10d[5/2]_3$

$16/34.15$ cm$^{-1}$

$5d[7/2]_3 \rightarrow 29f$

a)

b)
of these states with the 7p' state (Fig. 7). However, we have observed several d–p transitions which, to our knowledge, have not been reported before.
CHAPTER IV
1. **Introduction**

Having applied our RFLOG device to atomic xenon with considerable success, we next began the search for another atomic system to which our technique would be applicable. A search of the literature revealed that an early LOG investigation of cesium vapors in a DC discharge [57] yielded a rich absorption spectrum. We elected to repeat the investigation of cesium with our RFLOG device in an attempt to extend the observations on xenon to a second atomic system.

Cesium (atomic number 55) is an alkali metal with electronic configuration \([5p^6]6s^1\) (i.e., it possesses a single s electron outside of the "xenon core"). It exists as a solid at room temperature but melts at 28.59°C, slightly above room temperature. In order to obtain a sufficient vapor pressure to perform spectroscopic investigations on cesium, it was necessary to heat the cesium to a temperature of about 190°C at which cesium has a vapor pressure of about 50 mtorr [57]. Cesium was considerably more difficult to handle than xenon because of this requirement.

The spectra expected for an alkali metal are attributable to the single valence electron, the so-called optical electron, moving outside the inert noble gas core. The effective field in which this electron moves is centrally symmetric since the core has total orbital and spin angular momentum equal to zero. At large
distances, the effective field coincides with the coulomb field of charge e, because the electrons of the closed shell screen the nuclear charge. Thus, orbitals which lie far from the core are very much like the orbitals of hydrogen, and yield hydrogenlike spectra.

The energy of a line in the hydrogen spectrum is given by the expression:

\[ E = I - \frac{R}{n^2} \]

in which I is the ionization potential, R is the Rydberg constant for hydrogen, and \( n_1 \) is the value of principle quantum number of the terminating orbital. For hydrogenlike spectra, the energies of the spectral lines are given by a similar expression:

\[ E = I - \frac{R}{(n-\delta)^2} \]

in which \( \delta \), the quantum defect, is a measure of the departure of the state energy from that of a true hydrogen transition. The quantum defect is, to a good approximation, independent of \( n \), but dependent on \( \ell \) for the various transitions within an atomic species. The quantum defect is large for s-orbitals and smaller for p-orbitals. Moreover, the quantum defect is very small for the f-orbitals in cesium, indicating their extreme hydrogen-like nature.

The ground state term for cesium is \( ^2S \). The excited energy levels of the optical electron are all built upon the \( [5^6_p] 1S_0 \) core, and all series converge to the singly ionized \( 1S_0 \) state of
CsII, which corresponds to complete removal of the single s electron electron. All of the excited states, except for the excited s states, are split by the spin-orbit coupling of the optical electron. The energy levels are designated \( ^2L_{S} \) and \( ^2L_{S} \), in which \( L \) is the total orbital angular momentum (which is equal to \( \ell \), the orbital angular momentum of the optical electron) and \( S \) \((=\frac{1}{2})\) is the spin angular momentum of the optical electron.

The value of the spin-orbit interaction decreases with increasing \( \ell \): For the 6p states, the spin-orbit splitting is equal to 554.11 cm\(^{-1}\); for the 5d states it is 97.59 cm\(^{-1}\); and for the 6f states, it is 0.10 cm\(^{-1}\). (The splitting in the f-states is below the resolution of our equipment). The spin-orbit splitting also decreases with increasing \( n \). For example, compare the value for the 6p states with that of the 20p states, namely 1.59 cm\(^{-1}\)\([35]\).

With these values for the spin-orbit splitting in mind, one may speculate that the spectra expected from an experimental arrangement such as ours in the wavelength range of a rhodamine dye laser (1600-1700 cm\(^{-1}\)) should consist of doublets, representing the spin-orbit splitting of the lower states. Transitions within this range include (see Fig. 16) 5d-nf, 6d-np, 6p-ns and 6p-nd (\( n>8 \)). In all cases, the spin-orbit splitting of the lower state is appreciable, whereas the spin-orbit splitting of the upper state is small. The result is a doublet structure with a constant splitting, which reflects the splitting of the lower state, with the upper state either not showing any splitting by virtue of its own nature (s-states) or a very small unresolved splitting because of the size of \( n \) (nd, nf for \( n<8 \)).
FIGURE 16. Partial energy level diagram for cesium.
CsI, Energy Levels and Transitions Observed
In an early (1977) laser optogalvanic experiment, Bridges [57] used a continuous-wave laser to probe the spectral characteristics of a DC discharge in cesium vapors. He observed all of the transitions indicated in Fig. 16, thus demonstrating the remarkable sensitivity of LOG detection. He obtained up to a 30% decrease in operating voltage when the laser was tuned to resonance with certain transitions of the excited cesium atoms in the discharge tube.

More recent work on cesium using LOG detection was reported by Roesch [58]. Roesch was interested in detecting the parity-violating 6s-7s transition in cesium. He chose the LOG technique of Bridges because of its high sensitivity. Roesch proposed a two-photon experiment in which an IR laser was tuned to resonance with the 6s-7s transition, a second ring dye laser was used to promote the 7s electron to a high Rydberg state, (from which it was easily ionized by a subsequent collision), and the Cs II positive ions were detected by a thermionic detector. In order to perform the experiment, he first was forced to demonstrate that the ring dye laser could be stabilized to the 7s-np, n=12-18 transition using feedback based on LOG detection. With a discharge tube heated to 200°C and DC discharge, Roesch observed the 7s-np transitions and measured the hyperfine structure of the 7s1/2 - 14p3/2 transition. To date, the observation of the 6s-7s transition has not been reported but the results of the experiment demonstrate that the LOG technique can be used to stabilize the output of a ring dye laser to a specific frequency.

More recent experiments on cesium, not using the LOG technique,
have followed along two lines. First, experiments designed to obtain highly accurate measurements of cesium energy levels, ionization limits and quantum defects of nd and ns states have been performed [59-61]. Second, experiments designed to investigate the behavior of high rydberg states, experiments that exploit the highly hydrogenic nature of cesium rydberg states, have been performed in high magnetic fields.

As examples of the first line of investigation, Doppler-free two-photon spectroscopy has been used to investigate the transitions \( 6s+ns(n=0-54) \) and \( 6s+nd3/2, 5/2(n=7-53) \) [59,60]. A narrow-band dye laser was focused into a thermionic detector containing cesium vapor. The laser was reflected back through the detector and, by this means the two photon, Doppler-free effect was achieved. Wavelength measurement was accurate to one part in \( 10^7 \). The ionization limit was measured, and found to be \( 31,406.6476 \pm 0.0016 \text{ cm}^{-1} \). A non-monotonic variation in the quantum defect was detected [60] for the nd5/2 and nd3/2 series. The quantum defect peaks at about \( n=10 \) and decreases for higher states. The effect is small, being observed only under very high resolution, but is significant in that such a variation in quantum defect has never been reported for an alkali metal, and is as yet unexplained.

Another example of the first line of investigation concerning high precision measurements on cesium Rydberg levels, has been given by Goy, et al. [61]. These authors used a double resonance technique in the millimeter wave domain to measure transitions between adjacent Rydberg states in the ns and nd levels. They obtained new
information on the quantum defect in s, p, d, and f levels; fine structure in the p, d, and f levels; and hyperfine structure in the \( d_{1/2} \) and \( p_{1/2} \) levels for \( n = 23-75 \). These results provided a precise mapping of the cesium Rydberg states, and allowed the prediction of any transition between Rydberg states to an accuracy of about 1 MHz. Atoms were prepared in an atomic beam, and promoted to \( ns \) or \( nd \) states by a two-photon technique using an IR laser for the \( 6s_{1/2} \rightarrow 6p_{3/2} \) transition, or a green laser for the \( 6p_{3/2} \rightarrow ns \) or \( nd \) transition. Millimeter transitions were then induced between levels, and detection was accomplished by the field ionization method.

The second area of investigation deals with the behavior of high Rydberg states in a strong magnetic field. The high angular momentum states of cesium are very hydrogenic, as was mentioned above. In addition, these states are free from perturbation by channel interactions. These properties make the \( d \) and \( f \) states of cesium prime candidates for the study of Rydberg states in magnetic fields.

The absorption spectra of alkali and alkaline earth elements near their ionization limits in the presence of a magnetic field show peculiar patterns. They display a periodicity extending above the ionization limit, characterized by a regular energy spacing of \( 3/2(\hbar \omega_c) \), where \( \omega_c \) is the cyclotron frequency. These are called quasi-Landau resonances [62]. In addition, due to the \( n^4 \) dependence of diamagnetic susceptibility [56], the linear Zeeman effect will be
supplanted at moderate n (n>8) by a quadratic field dependence, and previously parity-forbidden transitions will begin to acquire intensity. At higher n values, the situation will be complicated further by progressive onsets of £-mixing and n-mixing, as well as by the various types of Landau resonances [56].

To study such phenomena, the atoms are produced in an atomic beam directed along the axis of an electromagnet. The atoms are excited by two photon laser spectroscopy [62,63] and detected by the ionization induced by a transverse electric field. The results of these and similar experiments, and their theoretical significance, are discussed in [62-64]. The experimental apparatus employed in the work presented in this dissertation does not have the capability of permitting extremely accurate measurements, in comparison to that described in [60-62]. We have, however, observed some evidence of £-mixing and autoionization in xenon, which we have attributed to the radiofrequency field produced in our RFLOG cell. We have consistently observed different spectra than those reported by other experimenters, who used DC discharges and longitudinal excitation in LOG studies. It is in the hope of observing new spectral features and in extending our observations on xenon that we have directed our attention toward the RFLOG investigation of cesium vapors.

2. **Experimental**

A quartz cell about 20 cm long and 8 mm in diameter was constructed with a ground glass joint on one end. The tube was
attached to a vacuum system consisting of a mechanical roughing pump and an oil diffusion pump. After allowing the tube to degas for several days, a small quantity (0.1 g) of cesium metal was placed in the cell, and the cell was reattached to the vacuum system. The tube and the cesium were thoroughly degassed and the cell was sealed under vacuum.

In order to attain sufficient vapor pressure to perform RFLOG studies on the discharge cell containing cesium, it was necessary to heat the cell, and to maintain a constant temperature throughout the experiment. To achieve a stable, high temperature, we constructed an aluminum oven (cf. Fig. 17). The oven was approximately 3" x 3" x 24". The discharge tube was mounted within the oven. Holes were drilled in the walls of the oven to allow the connections to the RF electrodes to enter the chamber, to allow the connection to the pick-up coil to enter the chamber, to allow the laser beam to penetrate the oven, and to allow the tip of a thermometer to protrude into the chamber. The source of heat was a hot-plate placed on the top of the oven.

This device could attain a temperature of 180 - 190°C, at which cesium has a vapor pressure of 50-60 mtorr [57]. Although it took about an hour to stabilize the operating temperature, this temperature, once attained, remained constant over time. Temperature control was provided by control of the hotplate.

In all other respects, the experiment was conducted as described in Chapter II.
FIGURE 17. Aluminum oven constructed to heat the cesium discharge tube.
3. Results

A typical spectrum of cesium vapor in an RF discharge is reproduced in Fig. 18. The various transitions observed are indicated in an energy level diagram in Fig. 16. The region accessible with rhodamine dye is $16,000 - 17,000 \text{ cm}^{-1}$. Within this range, transitions arising from the 5d and 6p states of neutral cesium are observed.

Four series arising from the 5d states have been observed. These are the $5d_{5/2} + nf_{7/2}$ ($n=12-30$), $5d_{3/2} + nf_{5/2}$ ($n=12-29$), $5d_{5/2} + np_{3/2}$ ($n=16-20$), and $5d_{3/2} + np_{1/2}$ ($n=17-20$). Also present are the transitions $6p_{3/2} + 8d_{3/2}$, $6p_{3/2} + 8d_{5/2}$, $6p_{1/2} + 8d_{3/2}$, and $6p_{3/2} + 10s_{1/2}$. The positions of the neon calibration markers are indicated in Fig. 18, along with the positions of the two 5d$+nf$ series as an index running horizontally across the top of the figure. The other peaks are identified individually.

4. Discussion

The spectrum reproduced in Fig. 18 is very similar to the one obtained by Bridges [57] using a DC discharge, continuous wave laser excitation, and axial excitation in a cylindrical discharge cell. No new peaks were observed by us, and only minor differences in intensities distinguish our results from the early LOG studies. There are some aspects of the spectrum, however, which deserve comment.

All of the transitions in Fig. 18 arise from the 6p and 5d states of cesium, which are populated by the RF discharge. In both
FIGURE 18. RFLOG spectrum of Cs in the range 16,000–17,000 cm$^{-1}$. 
cases, the transitions that are allowed by the parity selection rule are $\Delta \ell = \pm 1$. Thus, the transitions $p+d$ and $p+s$ are allowed, as are the transitions $d+p$ and $d+f$. In both cases, the transitions $\ell + \ell + 1$ are much stronger than the transitions $\ell + \ell - 1$. In the case of the transitions which arise from the $p$ states, the $6p3/2+8d5/2$ and $6p1/2+8d3/2$ transitions are so strong that the electronics were saturated, causing the peculiar attenuation of these two peaks is evident in Fig. 18. The $6p3/2+10g1/2$ peak is within the range of the electronics, and does not go off scale. The effect is even more pronounced in the case of the $5d+nf$ series, as compared to the $5d+np$ series. The two $5d+nf$ series show moderate intensity for $n=17-20$, whereas the $5d+np$ transitions for $n=17-20$ are barely discernable. These results are reminiscent of those obtained with xenon at low pressure (50-60 mtorr), in which it was consistently observed that transitions to higher angular momentum states were favored at low pressures, whereas transitions to the lower angular momentum states become dominant at higher pressures. An explanation for this observation is that the higher angular momentum states are more easily affected by increased collisional deactivation than are the lower angular momentum states, and thus begin to lose intensity as the pressure is increased.

The most interesting feature of Fig. 18 is the presence of the two $5d+nf$ series, in which $n=12+30$. The $5d$ levels are split by spin orbit coupling, with the magnitude of the splitting being 97.59 cm$^{-1}$. The result is that the splitting in the upper state is not resolved, and a series of doublets is obtained, each pair split by
97.59 cm\(^{-1}\), the energy difference between the 5d3/2 and 5d5/2 levels. The nf levels are also split by spin-orbit coupling, but the value of the splitting is only 0.007 for the 10f levels, and decreases with increasing n. This splitting is not detectable.

The two 5d+nf series are shown in Fig. 18, as they progress to their respective series limits. The 5d5/2+nf series converges to its limit of 16,809.63 cm\(^{-1}\). Members up to n=30 are discernible in Fig. 18. The intensity of each series member decreases as n increases. The peaks also become broader as n increases, as was observed for xenon.

Many attempts were made to obtain high quality spectra on cesium vapors. The experiment was complicated by the fact that the sample required heating in order to sustain a discharge. The discharge was not well behaved, in contrast to the case of xenon; indeed, it was unstable and very noisy. When wavelength dependent signals were obtained, they were always superimposed on a much larger background of wavelength independent noise. Signal extraction required delicate adjustment of the boxcar gate, which was very time consuming. Often, just as the adjustments were optimized, the characteristics of the discharge would change, and the process would have to be performed again from the beginning.

Another problem that continually arose was that the cesium vapors tended to condense near the lower region of the discharge tube (see Fig. 17). The holes which were drilled to allow the various wires, thermometer and the laser beam to enter the oven also allowed the entry of some air at room temperature. The cooling
effect of the air caused some condensation of cesium on the inner surface of the discharge cell in the region of laser excitation. The result was that some conduction of current occurred along the inner surface of the discharge cell, contributing to the large wavelength independent signal.

5. Conclusion

RFLOG spectra of cesium vapor have been recorded in the range 1600-1700 cm\textsuperscript{-1}. All transitions have been assigned. No new transitions were observed. The difficulties inherent in the experiment have precluded a detailed, high resolution study of cesium by the RFLOG technique. The most important lesson learned is that RFLOG experiments are most easily performed on species that exist in the gas phase at room temperature!
CHAPTER V
LASER OPTOGALVANIC SPECTROSCOPY OF NITROGEN

A. PREAMBLE

During the years 1980-1985 there has been a steady effort to extend the technique of optogalvanic spectroscopy from the realm of atomic spectroscopy to the realm of spectroscopy of small molecules [9]. A molecule which has proven to be particularly attractive for LOG studies is molecular nitrogen, N₂. Nitrogen is readily available in high purity, is easily handled in the laboratory, and the nature of its strong triple bond (i.e., the strongest covalent bond in nature) renders molecular nitrogen an ideal candidate for LOG studies. Thus, to the low chemical reactivity and high stability of N₂ in an electrical discharge suggest that N₂ should be an important test molecule for new LOG methodologies.

The spectroscopy of N₂ is interesting in its own right, as evidenced by the hundreds of papers which have appeared in the literature on this topic in the past decades. The nitrogen triple bond is very strong, as mentioned above. Due to the high bond dissociation energy (944.7 kJmol⁻¹), molecular nitrogen possesses bound states up to and exceeding 15 eV(120,000 cm⁻¹) above the ground state. At present, some 22 electronically excited states have been characterized and identified. However, a total of 102 electronic states should result from a combination of 2 nitrogen atoms, each in some one of its ⁴S, ²D, and ²P states [65,66]. Obviously, much work remains to be done on this interesting
molecule.

The first application of LOG spectroscopy to the study of molecular nitrogen was reported by Feldmann in 1979 [10]. Feldmann used a continuous-wave laser operating in the red region of the visible spectrum to probe a DC discharge in flowing nitrogen. The pressure was maintained at 200-500 mTorr. He observed absorption due to the familiar \( \text{B}^3\Pi \rightarrow \text{A}^3\Sigma^+ \) First Positive System, which is known to be conspicuous if not dominant in emission and absorption in most types of \( \text{N}_2 \) discharges. In addition, Feldmann observed the highly excited Rydberg state known as the Ledbetter Band \( (c^4 \Pi_u \rightarrow a^1\Sigma^+g) \) (see Fig. 19). His resolution, however, was Doppler limited and he was unable to resolve the lower rotational bands of the Ledbetter Band.

In 1981 and 1982, Suzuki [20] and Suzuki and Kakimoto [8] reported RFLOG investigations in which they employed a technique developed by Lawler [13] to obtain sub-Doppler measurements on molecular nitrogen. They utilized a narrow band, ring dye laser to probe an RF discharge in flowing nitrogen. The RF electrodes were positioned external to the quartz discharge cell. Changes in discharge impedance were monitored by an additional coil, one that functioned as an antenna and that was wrapped around the discharge cell (see Fig. 2). To obtain sub-Doppler resolution, the output of the cw dye laser was split into 2 equal portions. One beam was directed axially into the discharge cell from the right end, and the second beam was directed axially into the left end of the cylindrical discharge tube. The first beam was modulated by a mechanical chopper at frequency \( f_1 \) and the second beam was modulated
FIGURE 19. Potential energy diagram for nitrogen showing high-lying Rydberg states.
\[ \begin{align*}
B^3 \Pi_g &\leftarrow A^3 \Sigma_u^+ \text{(First Positive System)} \\
C_4 \Pi_u &\leftarrow a'' \Sigma_g^+ \text{(Ledbetter System)} \\
C' \Sigma_u^+ &\leftarrow a'' \Sigma_g^+ \text{(Suzuki and Kakimoto)}
\end{align*} \]

\[
\begin{array}{c}
C_4 \pi_u V=0 \\
C_2 \Sigma_u V=0 \\
\sigma'' \Sigma_g V=0
\end{array}
\]

\[
\begin{align*}
N(^4S^0)+N(^2D^0) \quad \text{or} \\
N(^4S^0)+N(^4S^0)
\end{align*}
\]

![Graph showing energy levels and internuclear distance](image-url)
in a similar manner at $f_2$. A lock-in amplifier was used to demodulate the LOG signal. When the LOG signal was demodulated at $f_1 + f_2$ or $f_1 - f_2$, sub-Doppler measurements could be obtained.

With the dual-beam, intermodulated techniques of Lawler [13] Suzuki and Kakimoto [8] succeeded in resolving the rotational structure of the Ledbetter Band. In addition, they observed a new Rydberg series arising from the $a''^1 \Sigma^+$ state and terminating on the $c^1 \Sigma_u^+$ state some 15eV (120,000 cm$^{-1}$) above the ground state. It is curious to note that in their RFLOG experiment using axial excitation, the First Positive System was entirely absent, which allowed the measurement of the weaker Rydberg series.

Convinced of the possibilities of obtaining important new spectroscopic information on $N_2$, we set about to apply our pulsed RFLOG device to the investigation of $N_2$. In the first experimental arrangement, similar to that used in the xenon experiments, we enclosed a sample of nitrogen gas inside a quartz discharge tube. Despite much effort and exhaustive manipulation of the experimental parameters, we were not able to obtain a wavelength dependent LOG signal. We then devised a flowing system in which crude control of the flow rate was provided by a stainless steel needle valve (cf. Fig. 20). A mechanical pump was used downstream from the elongated discharge tube to induce flow at low pressure. High-purity nitrogen was continuously supplied by a gas cylinder. Flow control was accomplished by the needle valve placed in-line between the nitrogen cylinder and the discharge tube.

After many hours of patient trial-and-error manipulation of
FIGURE 20. Diagram of the system designed to regulate the flow of \( \text{N}_2 \) through the discharge tube.
experimental parameters, we were able to achieve wavelength dependence of the LOG signal with some degree of repeatability. To perform the experiment, it was necessary for one experimenter to tune the laser and RF frequency while another worker manipulated the flow rate and locus of laser excitation of the discharge tube. After some time, we were able to recognize those discharge conditions that were favorable to our purposes, and to obtain results with less effort. The appearance of the discharge was the key factor in this regard. Only when the well known Lewis-Rayleigh Afterglow (emission from the First Positive System) was visible trailing downstream from the discharge tube toward the pump, and when an intense light-blue region was visible near the upper RF electrode (see Fig. 20), was it possible to obtain a wavelength dependent signal.

The spectra obtained from this arrangement were easily identified as due to absorption in the $\Delta v=4$ region of the First Positive System. Unfortunately, no new spectral features were observed. But, introducing an intracavity etalon, we were able to resolve the rotational structure under high resolution, and by remaining in a spectral region near our calibration markers, we were able to measure the positions of the rotational features to an accuracy of one hundredth of a wavenumber.

Although we had no new spectroscopic features to report, we were able to use our data to compare the rotational assignments measured by us with those measured by Dicke and Heath [67] in
emission and by R. D. Verma [76] on a 110 m Fourier spectrometer in the absorption mode. A comparison of these data allowed us to conclude that certain unidentified lines in the Johns Hopkins tables of Dieke and Heath [67] are not due to emission from the First Positive System. In addition, certain missing lines in the tables of Dicke and Heath were observed by our RFLOG technique. These results are presented in the next section.
1. Introduction

Nitrogen is the major constituent of the atmosphere. It is also one of the most spectroscopically investigated gases, a fact documented in hundreds of papers [68,69]. At present, some 22 electronically excited states of the neutral molecule have been characterized and identified. Three of them, namely $A^3\Sigma^+$, $B^3\Pi_{g}$ and $C^3\Pi_{u}$, are involved in the $B^3\Pi_{g}$+$A^3\Sigma^+$ and $C^3\Pi_{u}$+$B^3\Pi_{g}$ emissions, which are dubbed the First Positive System (35310A-4780A) and Second Positive System (5460A-2680A), respectively. However, a total of 102 electronic states should result from a combination of two separated N atoms, each in one of the $^4S^o$, $^2D^o$ and $^2P^o$ states [65,66]. Consequently, many new results, especially concerning high-energy excited states, are to be expected.

New methods for the production of atoms and molecules in such highly excited states are now available [70]. One of these methods probes a radiofrequency discharge in a low pressure gas with a tunable laser and records the resulting optogalvanic signal. This particular method is known as spectroscopy in radiofrequency discharge using laser optogalvanic effect (RFLOG) [2,8,32,42] and it possesses considerable promise. It consists of a closed or flowing gas sample; cw or pulsed laser excitation applied either in an axial orientation or in a transverse orientation at different points.
along the discharge; and an applied field of variable power and
frequency that sustains the discharge.

In this Section, we present RFLOG results for molecular
nitrogen, the purpose being to compare these with the emission and
absorption spectra of the First Positive System. This comparison
should lead to a resolution of the controversy concerning the use of
LOG signals for quantitative purposes --- a controversy that
originated in the apparent absence of any linear relation between
LOG signals and oscillator strengths [67, 71].

The existing literature may be summarized as follows:

--- The most extensive data available for the First and Second
Positive Systems, until recently anyway, were those of Dieke and
Heath [67] whose measurements refer to a low-pressure discharge
cooled with liquid nitrogen. Dieke and Heath also analyzed their
spectrum and extracted the molecular constants. However, these
constants referred only to the \( v = 0 - 8 \) levels of \( \Sigma^+ \) and the \( v = 0 - 12 \) levels of \( \Pi_g \) because of predissociation [10] in the \( \Pi_g \) state at all levels \( v > 12 \).

--- Cerny et al. [73] fitted their data for the \( \Delta_u - \Pi_g \) band
system (see Fig. 21) and obtained accurate molecular constants for
the \( \Pi_g \) state for \( v = 0 - 8 \).

--- Roux et al. [84] measured the First Positive System in the
emission mode between 3,000 and 18,000 cm\(^{-1}\) using a high-resolution
Fourier spectrometer. Thirty-three bands with \( 0 < v' < 12 \) and \( 0 < v'' < 8 \) were analyzed and the molecular parameters for the \( \Pi_g \) and
\( \Sigma^+ \) states were obtained.
FIGURE 21. Potential energy curves for low-energy states of neutral \( \text{N}_2 \).
Verma [75] measured the $B^{3}\Pi_{g} - A^{3}\Sigma^{+}$ system in the absorption mode using a flash discharge and an absorption path length of about 110 m. The analysis of the 12–8, 13–9, 14–10, 15–11, 13–8 and 14–9 bands was feasible at high resolution and molecular data for the $v' = 13, 14, 15$, and the $v'' = 9, 10, 11$ levels were extracted. Evidently, predissociation in the $v' > 12$ levels of the $B^{3}\Pi_{g}$ state is weak enough to permit observation of the higher levels. (Unfortunately, because of limitations inherent to our dye laser we have not been able to record the RFLOG spectrum above 17,300 cm$^{-1}$ and, therefore, we have not observed these higher-energy bands.)

Feldmann [10], who used a DC discharge and axial excitation in a laser optogalvanic (LOG) experiment in the range 16,300 to 17,600 cm$^{-1}$, did observe the First Positive System, including the 12–8 and part of the 13–9 bands.

It is also of some interest that, in the two remaining applications of RFLOG spectroscopy to nitrogen [8, 20] using cw laser excitation, the First Positive System did not appear. However, two different systems, the Ledbetter band $c_{4}(0) 1\Pi_{u} + a''(0) 1\Sigma^{+}$ and a new Rydberg band $(c'5 1\Sigma^{+} + a'' 1\Sigma^{+})$, were observed instead.

2. Results and Discussion

A 32 MHz RF discharge in flowing $N_{2}$ was probed transversely with a pulsed tunable laser [6] ($v = 16,300 - 17,300$ cm$^{-1}$) in the upper (light-blue) region of the discharge. The experimental setup is shown in Fig. 20. The resulting spectrum is clearly part of the First Positive System of $N_{2}$. This spectrum is shown at low
FIGURE 22. Low-resolution RFLOG spectrum of neutral $\text{N}_2$ from 16,300 to 17,300 cm$^{-1}$. The bandheads of the observed $\Delta v=4$ transitions of the First Positive System are indicated by arrows.
resolution in Fig. 22, where the bandheads of the observed \( \Delta v = 4 \) transitions are denoted, and a Ne calibration spectrum is also appended.

A small portion of this region, namely that surrounding the Ne marker at \( 16,996.61 \text{ cm}^{-1} \), was studied under high resolution (etalon of \( \sim 5 \text{ cm}^{-1} \) free spectral range). The recorded RFLOG signal is shown in the middle of Fig. 23. The peaks of the RFLOG spectrum are connected downwards to a stick spectrum of the First Positive System, as reported by Dieke and Heath [67]. The length of a stick is a rough measure of emission intensity. Since this region corresponds to the R side of the 9-5 transitions, members of only 17 of its 27 possible branches (see Fig. 24 for notation) are observed. We do not observe the branches \( P_{13}, Q_{13}, R_{13}, P_{11}, P_{12}, P_{22}, Q_{12}, P_{23}, Q_{23}, \) and \( P_{33} \). These either lie outside the spectral region or consist of members [74] with very high \( J > 20 \).

The members of the only branch, \( P_{13} \), of the 10-6 transitions present in the \( 16,996 \text{ cm}^{-1} \) region are identified by the encircled numbers 10 through 13. Some 25 lines reported by Dieke and Heath [67] are hardly, or not at all, observed in the RFLOG spectrum. These lines are unassigned and, therefore, they presumably do not belong to the First Positive System. These lines are indicated in Fig. 23 by a negative sign because no match exists between them and the upper RFLOG spectrum. In addition, lines which were not reported by Dieke and Heath [67] were observed at \( 16,997.65, 16,999.03, 16,999.22, 17,003.39 \) and \( 17,017.10 \text{ cm}^{-1} \) in the RFLOG spectrum.
FIGURE 23. Correlation of the high-resolution RFLOG spectrum of $N_2$ with its emission spectrum, as represented by a stick diagram.
FIGURE 24. The 27 possible P, Q, and R branches corresponding to $\Delta J = -1, 0, \text{ and } +1$, respectively, of the $^{3}I_{G} \leftrightarrow ^{3}E^{+}$ transitions from/to an upper state of a given $K'=2$. The selection rules $\Delta J=0, \pm 1$ and $\Delta K<3$ apply. Subscripts 1, 2, or 3 are used to designate spin states of upper and lower electronic states for which $J=K+1$, $K$, or $K-1$, respectively.
These are indicated by a broken line ending in a positive sign. Thanks to Dr. R. D. Verma [76], who sent us unpublished results for the observed lines and their assignments as obtained from absorption measurements of the First Positive System in this region (the 9-5 band), the Verma lines, those reported by Dieke and Heath, as well as ours can be assigned. These assignments are given in Table 2, where unresolved lines are enclosed in braces. The positions of those calculated lines that are not observed in absorption are given in parentheses. Lines observed in the RFLOG spectrum are indicated by √ and + signs, the latter describing those lines which were not observed in emission.

It is noteworthy that all RFLOG lines are now assigned and that those nonexistent in the Dieke and Heath spectra are also part of the First Positive System (+ lines). On the other hand, the additional, unassigned lines in Dieke and Heath are evidently not members of this system but arise instead from some other emission source (or emitting state). The observed RFLOG intensities and the rough estimates of emission intensities given by the length of the sticks correlate quite well.

In our opinion, the main reason for the different sets of observations in the various LOG experiments arises from excitation of a discharge in which different populations of absorbing species exist at different discharge points. Another complication is introduced by the fact that, for excitation between the discharge electrodes, both positive and negative signals may be generated by
### TABLE 2

Comparison of Emission, Absorption and Optogalvanic Spectrum of the Nitrogen First Positive System from 16992 - 17026 cm$^{-1}$

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<th>Assignment**</th>
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*Dieke and Heath [67]  
Verma [76]  
(Present Work)
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* See also Fig. 4 and text for details

** Members of the 10-6 band are encircled
excitation in different discharge regions. In our small tube (5 mm diameter) and with our transverse excitation modality (excitation outside the electrodes), this possibility is greatly reduced.
CHAPTER VI
A. PREAMBLE

As mentioned in Chapter I, conventional methods used to carry out photoacoustic measurements on gases using a small microphone as the sonic transducer suffer from significant disadvantages. First, microphones are not applicable to studies at low (i.e., less than 1 torr) pressure. This can be a significant limitation if one is interested in the study of predissociations or level crossings, which may be obscured by collisional events at pressures greater than a few hundred millitorr. Second, microphones are not applicable to the study of corrosive or reactive gases which may attack the surface of the microphone. As an example, Chuang and Zare [28] found that a microphone was destroyed by radioactive decay when they tried to measure the overtone spectrum of HT. As another example, Kumar (unpublished data) experienced a similar problem when a microphone was used to study Cl2. Third, microphones cease to function at high temperatures.

Efforts have been made to overcome these problems with contactless sensors [26,27]. Zapka, et al. [27] developed a method to monitor the PA signal arising from pulsed laser excitation of a flame. A cw probe laser was directed through the flame and onto a detector consisting of a fast photodiode. A knife edge was used to block half of the probe laser beam. The acoustic wave resulting from the pulsed excitation laser propagated outward and the arrival of the acoustic wave at the region of the cw probe laser was marked by a transient deflection of the probe laser beam. This

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deflection was easily detected as a change in the amount of light striking the photodiode. Time-resolved studies using this technique permitted the performance of accurate temperature measurements on flames.

Frequency resolved spectra were obtained by Chuang and Zare [28] on CH$_3$OH, a material which causes surface decomposition of a microphone. In their device, which they termed an "optophone", a thin nitrocellulose membrane was placed between two chambers of a cell containing the gas under study at equal pressures. A cw probe laser beam was directed onto this thin pellicle, and the reflected beam was focused onto a position sensing detector. A modulated cw excitation laser was directed into one chamber containing the test gas. The acoustic wave generated by the excitation laser beam induced vibrations in the thin pellicle, which caused spatial deflection of the probe laser. The authors claim sensitivity equal to that of a microphone in their study of the 5-0 O-H overtone of CH$_3$OH.

Other contactless techniques have been developed [29,30]. These methods are also based on a transient change in refractive index induced by the absorption of a pulsed laser beam. This "thermal lensing" technique has the advantage of rapid time response, but has not been used to obtain frequency resolved spectra, at least so far as we know.

In this Chapter, we report a new technique for obtaining photoacoustic spectra of low pressure gases. This technique, which we
call "PARFLOG", is a modification of our RFLOG technique. PARFLOG employs the same apparatus used to perform RFLOG measurements. The only difference is that the laser beam is directed several centimeters below the discharge region. The PA signal produced by pulsed laser excitation travels up the discharge cell and causes a mechanical perturbation of the discharge. The signal is picked up as a change in RF power delivered to the pick up coil.

PARFLOG has several advantages over conventional methods of obtaining PA information. First, the technique is applicable to gases at very low pressure (100 mtorr or lower). Second, the technique is contactless, which allows for the study of corrosive gases. The only limitation of PARFLOG is that the gas under study must be stable in the RF discharge, and even this limitation can be overcome by a suitably modified flowing system.

We have applied the PARFLOG technique to the study of magnetic field induced level crossings in molecular iodine. By recording the spectrum in the absence of any magnetic field, and in the presence of a 12 kG magnetic field, we have measured differences in the photoacoustic spectrum attributable to magnetic-field-induced predissociation. The magnetic field was obtained by placing the absorption cell between the pole pieces of a large magnet. These results are presented in Section B of this Chapter. Section C of this Chapter assesses the sensitivity and linearity of the PARFLOG technique.
B. PARFLOG: A NEW TECHNIQUE FOR LOW-PRESSURE PHOTOACOUSTIC SPECTROSCOPY. MAGNETIC PREDISSOCIATION OF THE I₂ B-STATE

1. Introduction

Photoacoustic (PA) spectroscopy has evolved into a multiple-use, sensitive detection technique [77]. In particular, its use in the study of nonradiative processes, ones which may or may not convert absorbed optical energy into vibrational/translational motions, promises to be informative.

In gas phase investigations, the initial PA disturbance, which is a pressure wave, is sensed by a microphone. Thus, minimal gas pressures requisite for efficient signal transfer to the microphone must exist. Unfortunately, these minimal pressures, not to speak of moderate or high pressures, may cause excessive collisional perturbation of the absorbing molecules, with the result that they "swamp" the intramolecular process of interest. Hence, the ability to prosecute low-pressure photoacoustic measurements is a prerequisite for studying such processes as level-crossings, predissociations, field effects, etc.

The limiting factor is the reduced sensitivity of the microphone at lower pressures, the inertia of the diaphragm being the primary culprit. Obviously, elimination of the microphone and detection of the acoustic wave at the molecular or atomic level would provide the ideal solution to the low pressure detectivity problem. Fortunately, such a detector exists: a low-power
electrical discharge in a low-pressure gas serves admirably as an
acoustic wave sensor [25]. The DC discharge method of Rettner, et
al. [25], however, is both insensitive and experimentally awkward.
In particular, the use of internal electrodes inhibits the ability
to perform measurements on corrosive gases. The solution to both
difficulties lies in the use of external electrodes. Thus, in what
we believe to be an original variant of the radiofrequency (RF),
laser-optogalvanic (LOG) technique [78], we have developed a new,
sensitive method for detecting photoacoustic (PA) signals. We refer
to this technique as PARFLOG. This PARFLOG technology is applicable
at considerably lower gas pressures, to all atoms and molecules
which do not decompose in (and thus do not contaminate) a low power
(\(\sim 1 \text{ W}\)) RF discharge. However, even this limitation can be overcome
in a suitably modified flow system.

The observed fluorescence lifetime \(\tau_{\text{obs}}\), as measured after
excitation by a laser pulse, is

\[
\frac{1}{\tau_{\text{obs}}} = \frac{1}{\tau_f} + \frac{1}{\tau_{\text{nr}}} \tag{1}
\]

where \(\tau_f\) and \(\tau_{\text{nr}}\) are radiative and nonradiative lifetimes,
respectively; and

\[
\frac{1}{\tau_{\text{nr}}} = \sigma_s \frac{16\pi \hbar^2}{\kappa T^2} p + \sigma_g \frac{8\pi \hbar^2}{\mu k T} p_g + b H^2 \tag{2}
\]
where the terms on the right represent, in order, self-quenching, foreign gas quenching and magnetic field induced contributions, respectively. The quantities $\sigma_s$ and $\sigma_g$ represent, respectively, self and foreign gas collisional quenching cross sections for iodine fluorescence; $P_i^2$ and $P_g$ represent the pressures of iodine and the foreign gas, respectively; $m$ is the mass of the iodine molecule; $\mu$ is the reduced mass of the iodine molecule and the foreign gas colliding partner; and $b$ is a constant which relates the influence of magnetic field $H$ to the fluorescence quenching [79].

When applicable, additional terms may be added to the right hand side of Eq. (2). For example, electric field quenching, spontaneous internal conversion, etc. may have to be included. Only that part of the absorbed energy which is diverted into the fluorescence channel departs the system; all of the remaining energy must eventually be converted into a photoacoustic signal. (This is true provided no photochemistry takes place.)

The ability to discriminate the magnetic field-induced predissociations (i.e., the $bH^2$ term) requires that the other terms in Eq. (2) not be dominant in comparison to $1/\tau_f$. In other words, if $1/\tau_{nr} >> 1/\tau_f$ there will be little or no fluorescence and virtually all of the energy absorbed from the laser pulse will revert into the PA channel. In such a case, the imposition of a magnetic field will not induce any alteration of the PA signal (unless, of course, it produces an actual change of the absorption spectrum). It is known that magnetic fields do not affect the B+X
absorption spectrum of iodine [79]. Yet, the PARFLOG spectrum at
~200 mTorr does exhibit magnetic field perturbations which are
immediately attributable to a field-induced predissociation of low
vibrational levels (v' ~ 6) of the iodine B-state.

The magnetic field-induced predissociation of the iodine
B-state has been measured for low v' by fluorescence quenching
techniques [79-82]. An 0 state was originally presumed to be
responsible for the magnetic predissociation of the iodine B-state,
but Vigue, et al. [82], having detected the presence of interference
effects between the magnetic and natural predissociations, concluded
that a single \( ^1\Pi_{\text{lu}} \) state was causing both predissociative events.
They also extended the lower limit of v' from 6 to 4 and showed that
the value of the parameter b was maximal at v' ~ 5. Now, the
low-pressure PARFLOG technique is readily applicable to the iodine
molecule and, as emphasized earlier, the ability to perform
low-pressure PA spectroscopy not only permits detection of magnetic
field induced predissociation in \( I_2 \), but also reveals differences
between the zero-field absorption and PA spectra that are
attributable to variations of the fluorescence quantum yields from
the different vibrational levels of the B-state.

2. Experiment and Results

The RF generator/signal pick-up system is shown in Fig. 25.
The sample cell consists of a closed quartz tube (~6 mm i.d.) which
is thoroughly degassed before and after encapsulation of a small
piece of solid iodine. The vapor pressure is readily controlled by
cooling the tube end which contains the solid iodine. External copper electrodes, separated by a few centimeters, are wound onto the quartz tube and the RF discharge is excited through the impedance matching network. The sonic disturbance, generated as shown in Fig. 25 by a transverse laser pulse (~1 μs, 10 Hz repetition rate, 2-4 mJ per pulse), propagates into and perturbs the RF discharge. The RF discharge itself extends beyond the electrodes and into the region of the pick-up coil. The pulsed change in the RF power, as transmitted to this coil, constitutes the PA signal.

This particular use of an RFLOG technique (as well as the RF LOG technique itself, at least as induced by pulsed lasers [6]) is unique.

A novel pulse treatment procedure [29], one based on simple analog circuits, has been used to normalize the signals on a pulse-by-pulse basis and to force the effective signal duty cycle toward unity. This procedure yields smooth, high resolution spectra even at low pulse-repetition rates. The wavelength calibration markers, generated using the optogalvanic effect in a hollow cathode lamp (neon filler gas), are displayed on the second channel of an x-y recorder (upper trace in Fig. 26) and permit precise calibration of the spectrum.

The absolute sensitivity of the technique is hard to determine because of the loss of absorbed energy through fluorescence. However, comparison of the gas phase absorption data for I$_2$, as obtained using a Cary 14 spectrophotometer, with values of the laser energy per pulse gives an estimated absorption detectivity of
FIGURE 25. Set-up for extracting PARFLOG signals.
RF OSC
-32 MHz

POWER AMP

SIGNAL RECOVERY

TO BOX-CAR

AMP

LASER
FIGURE 26. PARFLOG spectrum of iodine vapor at 20°C. Laser band width ≈3 cm⁻¹ at 10 z repetition rate. Upper trace shows neon wavelength calibration markers.
approximately $10^{-8}$ J per pulse. Since an unknown fraction of this energy is lost in fluorescence, the PA detection sensitivity of the RF discharge sensor must be better than $10^{-8}$ J per pulse.

The PARFLOG spectrum of I$_2$ vapor at 20°C in the region 16,200-17,200 cm$^{-1}$ is shown in Fig. 26. The laser bandwidth of $\sim 3$ cm$^{-1}$ is inadequate to resolve the rotational structure which is barely discernible in this figure. Fig. 27 shows a small region (16,992-16,997 cm$^{-1}$) around the neon calibration marker at 16,996.61 cm$^{-1}$, as recorded with an intracavity etalon ($\Delta v \approx 0.1$ cm$^{-1}$). This spectrum reveals the rotational structure of the B$\rightarrow$X transition. Even at moderately low laser power (4-5 mJ for the Rhodamine 6G dye), these spectra exhibit an excellent signal/noise ratio. They are presented here merely to illustrate the sensitivity of the technique. Magnetic fields produce no significant effect in this spectral region.

Fig. 28 shows a typical high resolution ($\Delta v \approx 0.1$ cm$^{-1}$) PARFLOG spectrum in the region of interest at low $v'$ values ($v' \approx 6$) where magnetic field induced predissociation is strong. Fig. 28(a) refers to H=0, whereas 28(b) refers to a transverse field H $\approx$ 12 kG. The low power of the laser ($\sim$1 mJ) produces a somewhat noisy spectrum; yet, despite this, field-induced spectroscopic changes are quite evident.

3. Discussion

The low laser power and the weak B$\rightarrow$X absorptivity in the 634 nm region causes the spectrum of Fig. 28 to be noisy. Moreover, the
FIGURE 27. High resolution ($\Delta \nu \approx 0.1 \text{cm}^{-1}$) PARFLOG spectrum of iodine vapor at 20°C. The upper trace shows the neon calibration marker at 16,996.61 cm$^{-1}$. 
FIGURE 28. Magnetic field effects on high resolution ($\lambda \approx 0.1 \text{ cm}^{-1}$) PARFLOG spectrum of iodine vapor at 20°C. The spectra refer to (a), a zero external field and (b), a 12 kG field.
TABLE 3

Calculated\(^a\) values of I\(_2\) line frequencies and intensities (B+X absorption) for the peaks shown in Figure.

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\(^a\)Calculated from molecular constants provided in [83] and [84] (only stronger components are listed).
laser resolution, even with the intracavity etalon, is inadequate to resolve all of the rotational structure, particularly in this transition region where several v'-v" active pairs are extensively overlapped. Hence, Fig. 28 contains mostly envelopes of two or more closely spaced or overlapped lines and, occasionally, some isolated transitions. The prominent peaks of Fig. 28 are numbered 1 through 10. Their constituent components are listed in Table 3 with the frequencies and relative intensities being calculated from molecular constants and Franck-Condon factors given by Luc [83], and Tellinghuisen [84], respectively.

The net photoacoustic signal consists of several processes: rovibronic relaxations in the upper and lower electronic states, fluorescence, collisional deactivation and dissociation (including predissociation). At lower pressures, where collisional deactivation is not dominant, fluorescence and (pre)dissociation can compete with the other processes and the PA signal, to the extent that the recombination of the dissociated fragments is slow, can exhibit a decrease. On the other hand, if a strongly fluorescing state is coerced into predissociation by some external perturbation, an increase of PA signal should occur. Indeed, depending on the characteristics of the molecular system and the excited states involved, an increase or decrease of PA signal strength can result from induced predissociation.

In the case of the magnetic field induced predissociation of the B-state of I₂ at 20°C, we find that the imposition of a 12kG magnetic field produces a larger reduction of the PA signal from v'=6 than that from v'=7 or 8 (see peaks 1, 3 and 9 of Fig. 28,
which originate solely or largely from $v' = 6$). Because of a lack of laser power and resolution, these measurements could not be extended to $v' < 6$.

Fig. 28(a) and Table 3 demonstrate that absorption intensities do not match photoacoustic intensities. For example, the calculated absorption intensities for peak 4 (for all components, see Table 3) is roughly half of that for peak 5, whereas the photoacoustic intensities are nearly identical. This implies that radiative loss from $v' = 8$ is greater than that from $v' = 7$ or 6. The fact that $v' = 6$ and 7 are more predissociative (natural predissociation) than $v' = 8$, and that in this case predissociation reduces the FA signal (as seen by application of a magnetic field), implies that the energy loss in $v' = 8$ is greater than would be deduced from direct comparison of photoacoustic intensity of peaks 4 and 5.
C. RF DISCHARGE: A LOW-PRESSURE, CONTACTLESS SONIC WAVE SENSOR

1. Introduction

The standard sensor for acoustic waves in gases is a microphone. The inertia and the elastic properties of the diaphragm, even at atmospheric pressure, not only delay the generation of the electrical signal but also introduce a complex impulse response in the transducer function. A conventional microphone at low pressure, obviously, will have even more adverse characteristics. Indeed, conventional microphones generally lose their sensitivity as the pressure of the gas is reduced, the primary culprit being the inertia of the microphone diaphragm. Minimal gas pressures, of course, are necessary for efficient signal transfer and, at very low pressures, where the mean free path of the gas molecules may become as large as, or even larger than the size of the enclosure, the acoustic wave, being a collective phenomenon, may lose definition altogether.

In this Section, we provide further details on a low-pressure, contactless, acoustic wave sensor which, under suitable conditions, can act as an excellent substitute for the conventional microphone. The only restriction on the use of this detector is that the pressure of the gas be low enough to sustain an RF discharge (i.e., a few torr or so) and that the gas be stable enough under discharge conditions that it does not contaminate the system. However,
even this latter restriction can be alleviated in a suitably modified flow system.

2. The Acoustic Wave Sensor

The block diagram of the acoustic wave sensor is shown in Fig. 25. A low power (~1 W) RF (~32 MHz) discharge excited in the gas by external electrodes wound a few centimeters apart on a quartz tube of 8mm diameter is used as the detector of acoustic waves inside the tube. Higher RF power, or a tesla coil, is needed to initiate the discharge. The power amplifier can generate as much as ~20 W which, via the intermediacy of a resonant step-up transformer, converts into several thousand volts. The heart of the sensor consists of a pick-up coil of a few turns wound around the tube at a separation of 5-10 mm from one of the electrodes. This resonantly tuned pick-up coil is coupled to the RF discharge which extends beyond the electrodes. The acoustic wave that propagates through the region between the pick-up coil and the electrode modulates the RF power transference to the pick-up coil. This modulation, which is extracted in the signal recovery section, constitutes a replica of the acoustic signal. It should be noted that no membranes or diaphragms need be displaced by the acoustic wave and that the signal is picked up on a molecular (or atomic) level. The signal, therefore, should be free from most of the inherent drawbacks of conventional microphones (i.e., limited frequency response and distorted impulse response).

The characteristics of this sensor may be studied by
introducing a source of acoustic waves to the inside of the tube. However, for studying fast-impulse response, it may be preferable to generate the acoustic impulse, via the photoacoustic effect, with a short-duration pulsed laser.

In prior work, described in the previous Section, this acoustic wave sensor was used to carry out low pressure photoacoustic spectroscopy of iodine molecules. The pulsed sonic wave was generated by the photoacoustic (PA) effect in a region excited by a pulsed tunable dye laser (see Fig. 25). This detection technique was termed "PARFLOG" (Photoacoustics using Radio Frequency Laser OptoGalvanic detection) because it was merely a variation of the usual laser-optogalvanic (LOG) effect [17]. The pulsed sonic wave necessitates the use of a boxcar integrator for signal reception. However, a lock-in amplifier may be used with cw sonic sources, which is of help in eliminating most random discharge noise.

The pulsed signal picked up by the boxcar integrator is normalized with respect to the incident laser energy in the particular pulse, and these normalized signals are subsequently averaged over successive laser pulses. This procedure is carried out using a special analog technique which, as described earlier [31], forces the effective signal duty-cycle to approach unity.

3. Discussion

Though implicit in earlier Chapters, we did not emphasize
the linearity, frequency response or other important characteristics of the sonic detector.

The acoustic wave (transient) is generated by the photoacoustic effect that follows the excitation of iodine molecules \((B + X)\) by a pulsed laser. The measurements, therefore, are restricted to transient acoustic waves only: That is, \(cw\) measurements cannot be performed. Consequently, we could not assess the acoustic frequency response of our detector. However, since the acoustic wave is picked up on the molecular level (i.e., without any mechanical device), the acoustic frequency response is expected to be determined by the intermolecular collision frequency (i.e., the response will be dependent on the mean free path and rms velocity of iodine (or other gas) molecules/atoms). For iodine at \(\sim 200 \text{ mTorr and } 20^\circ \text{C}, this upper frequency (say 1/10th the intermolecular collision frequency) is estimated to exceed 100 kHz. This value far exceeds the response of conventional microphones, even at atmospheric pressures. This upper frequency limit will increase further with increasing gas pressures. The RF frequency need not be a limiting factor, since it can easily be increased from the 30 MHz to the GHz range using microwave sources.

The amplitude response is found to be linear over at least three orders of magnitude of the acoustic wave intensity. This linearity range is estimated as follows:

(i) The generated signal is found to be proportional to the laser energy (i.e., to the acoustic wave intensity because of the linear energy dependency of the PA signal) over two orders of
magnitude of laser energy.

(ii) The change of laser wavelength (\(\approx 3\ \text{cm}^{-1}\) bandwidth) from approximately 17,200 cm\(^{-1}\) to 16,200 cm\(^{-1}\) causes a decrease of the actual PA signal in iodine vapor by an order of magnitude. However, since the iodine PA spectrum recorded in this region using our sonic detector (see Fig. 26) is an exact match of that recorded with a conventional microphone operating at somewhat lower pressure, we can safely assume that our sonic detector exhibits an additional order of magnitude linearity in its amplitude response. The total range of linearity of amplitude response, therefore, is at least three orders of magnitude.

A rough estimate of the minimum detectivity of the sensor (i.e., the minimum energy required to generate a signal over and above the noise level) is also available. The comparison of gas phase absorption data for \(I_2\), as obtained using a Cary 14 spectrophotometer, with the laser energies per pulse yields an absorption detectivity of \(\approx 10^{-8}\) J per pulse for laser excitation at a point that is a few centimeters removed from the discharge region. For laser excitation close to the discharge region, the absorption detectivity is even better (\(\approx 10^{-9}\) J per pulse). It should be noted that all the energy absorbed from the laser pulse is not used in the production of an acoustic signal. An unknown fraction of this energy is lost to fluorescence and, hence, the values mentioned above are upper limits for the acoustic energy detectivity. This is an important characteristic, one that must be emphasized. Our
acoustic wave sensor easily picks up the signals (PARFLOG, see Fig. 26) from I\textsubscript{2} vapors at \textasciitilde 200 mTorr, whereas a conventional electret microphone (Knowles Electronics BT1759) failed to pick up any acoustic signal under similar conditions. The delay between optical excitation and the generation of the signal in the sensor (Fig. 25) depends linearly on the distance between the point of optical excitation in the tube and the RF electrode. Indeed, the slope of this linearity accords with the velocity of acoustic waves in the particular gas.

The linear dependence on distance and sound velocity in the particular gas was also observed by Rettner, et al. [25], who used internal electrodes and a DC discharge method for detecting acoustic waves. The Rettner system is somewhat insensitive because the whole discharge has to be disturbed in order to generate the signal. Moreover, because of the internal placement of electrodes, it cannot be used with reactive/corrosive gases.

Another interesting feature of our system involves the generation and detection of acoustic waves under conditions such that the laser beam is incident on the extended discharge between the pick-up coil and the nearer electrode. The variation of the signal delay with distance of excitation from the electrode (lower, Fig. 25) indicates that the sensor picks up the signal not when the acoustic wave reaches the pick-up coil, but when it reaches the lower electrode. This observation may be used to study the acoustic properties of the plasma generated in the discharge itself.
The linearity of the response over large variations of acoustic wave intensity and frequency, and the pressure dependency of the response are still to be assessed completely. However, there is no doubt that the RF technology provides an excellent alternative to the conventional microphone, particularly when gas pressures are low.

The RF discharge might be expected to make the system noisy. However, the use of low RF powers (1 W or less) makes this noise insignificant. Gated electronics for pulsed sources and lock-in amplifiers for cw sources also facilitate the extraction of clean signals.
CHAPTER VII
TIME-RESOLVED LASER OPTOGALVANIC SPECTROSCOPY
OF IODINE

1. Introduction

The mechanisms involved in the production of the optogalvanic effect in atomic and molecular systems have elicited much interest.

In the case of atomic systems [85-87], direct ionization processes are deemed responsible for the maintenance of the electrical discharge. These processes include associative ionization \((A+A^* + A+A^+e^-)\) and electron impact ionization \((A+e^- + A^+2e^-)\). It is generally agreed that an optogalvanic effect occurs when the laser populates excited atomic states that lie near the ionization threshold and that are easily ionized by a subsequent collision. The immediate result is an increase of discharge current, and production of a positive optogalvanic signal.

In the case of molecular systems, processes such as collisional ionization are undoubtedly essential for the maintenance of an electrical discharge. Indeed, it seems reasonable to suppose that the ionization rate depends upon the degree of electronic excitation, much as in the case of atomic systems. This supposition is inadequate, however, in two respects. First, it fails to explain how the optogalvanic effect is produced by low energy infrared photons [88,89] which, when absorbed, result in vibrational rather than electronic excitation. Ionization rates are
expected to be quite insensitive to the level of vibrational excitation but very sensitive to the degree of electronic excitation. Second, it fails to explain how the optogalvanic effect can be produced by laser excitation in a region of the discharge that is removed by considerable distances (up to 40 cm [90]) from the region of electrical discharge.

A theory which purports to explain these two phenomena has been given by Haner, et al. [90]. They interpreted the optogalvanic effect produced by remote excitation of a DC discharge in I₂ vapor with visible laser radiation in terms of a pressure pulse which traveled through the gas to the discharge region, and which, by virtue of simple kinetic effects, caused a perturbation of the electrical discharge. The pressure pulse was attributed to the dissociation of molecular iodine (I₂ → 2I), and to the inelastic repartitioning of energy between vibrational and translational motions (V-T transfer), with kinetic energy increasing at the expense of vibrational energy. The optogalvanic effect produced by IR radiation was explained as follows: The energy deposited in the vibrational modes was supposed to degrade to kinetic energy by V-T transfer, producing a "heating effect". That is, collisional ionization was thought to be promoted by an increase in the average kinetic energy of the molecules that mediate the electrical discharge.

In a time-resolved study of the optogalvanic effect in I₂ vapor, Haner, et al. [90] measured the speed of propagation of the pressure pulse initiated by remote visible laser radiation.
They demonstrated that the pulse traveled at the speed of sound. We have also recorded frequency-resolved spectra using remote excitation of a radiofrequency discharge in iodine vapors (see Chapter VI) and have demonstrated that the excitation spectrum for the "pressure pulse" is photoacoustic in origin. That is, comparison of spectra recorded by the radiofrequency laser optogalvanic (RFLOG) technique using remote excitation, with spectra recorded in a conventional photoacoustic (PA) cell (i.e., with a microphone being the sonic transducer) were identical. These results confirm that the optogalvanic effect in I$_2$ is mediated by a photoacoustic effect and that it involves a degradation of the energy deposited in electronic modes into translational energy through inelastic collisions, collisional deactivation of molecular excited electronic states and by molecular dissociation into atomic iodine.

Previous attempts to explain the optogalvanic effect in molecular systems, such as I$_2$ [90,91], were complicated by the nature of the DC discharge that was used. Such discharges are characterized by discrete, distinguishable discharge regions (e.g., the "negative glow" region). Laser excitation yields an optogalvanic signal which may even change sign when different discharge regions are excited. In order to explain such negative signals, processes such as electron attachment (I$_2$+e$^-$+I$_2^-$) have been advanced in order to account for decreases in discharge current upon laser excitation. In our variation of the RFLOG technique, we observe optogalvanic signals which do not change sign as the
discharge region is traversed by the laser beam. One immediate advantage of this observation is that future optogalvanic models will not have to account for negative optogalvanic signals and processes such as electron attachment may be excluded.

We report here the results of a time-resolved study of iodine vapors in a radiofrequency discharge subject to pulsed laser excitation directed into the discharge itself, coupled with laser optogalvanic detection. The results indicate the presence of two optogalvanic signals. The "fast" signal arises from dissociated iodine atoms in excited electronic states. The "slow" signal results from absorption by iodine molecules in the ground electronic state. The spectra of the molecular signal appear to be identical to those obtained with a conventional photoacoustic cell in which a microphone transduces the photoacoustic signal. The time evolution of the two optogalvanic signals is discussed in terms of the simple mechanisms that are active in the production of the optogalvanic effect in atomic and molecular systems. It is shown that a model which considers only collisional ionization rates, and the dependence of these rates on (a) the degree of electronic excitation of the entities participating in the collisions and (b) the local temperature or average kinetic energy per collision, is sufficient to explain the results.

2. Experimental

The experimental arrangement for RFLOG measurements has been shown previously (cf. Fig. 4). The sample is contained in a quartz
discharge cell 8 mm in diameter and 30 cm long. Two copper
electrodes, wound around the exterior of the cell, are positioned
about 5 cm apart. A radiofrequency oscillator and amplifier serve
as a 33 mHz source of RF power for the external electrodes.
Approximately 1 W of RF power is sufficient to sustain a stable, low
noise discharge in I₂ vapor at 200 mtorr.

A pick-up coil, also wound around the discharge cell, is
situated ~1 cm below the lower RF electrode (cf. Fig.4). The output
of a pulsed, tunable dye laser impinges transversely on the cell at
a point between the lower RF electrode and the pick-up coil. When
the laser is tuned through a frequency resonant with some species in
the discharge, a change occurs in the power of the discharge. This
change in discharge power produces a change in the power transferred
to the pick-up coil and constitutes the optogalvanic signal.

A boxcar intergrator is used as a gated detector to monitor the
optogalvanic signal. Both the delay between the laser pulse and the
boxcar gate, as well as the duration of the gate, may be adjusted in
order to monitor any time segment of the response of the discharge
subsequent to laser firing.

A novel pulse treatment procedure [31,32] based on simple
analog circuits is used to normalize the signal on a pulse-by pulse
basis and to force the effective duty-cycle toward unity. This
procedure yields smooth, high-resolution spectra even at low
pulse-repetition rates.

Wavelength calibration markers are generated by diverting about
5% of the laser beam into a hollow cathode lamp that contains neon
as a filler gas. When the laser is tuned through an absorption frequency of some species in the lamp, a pulsed change in lamp voltage is produced (i.e., the optogalvanic effect occurs). This voltage pulse is monitored across a series resistor and, when amplified, is recorded on the second channel of an x-y recorder.

3. Results

With the experimental configuration depicted in Fig. 4, we have observed two optogalvanic signals subsequent to each laser pulse. The fast signal is essentially synchronous with the laser pulse and is quite short (~3 μs). The slow signal initiates some 200 μs later and lasts about 250 μs. As the locus of laser excitation is moved downward in Fig. 4, to a region below the discharge, the fast signal disappears and the delay in the slow signal increases. In fact, the delay of the slow signal increases in direct proportion to the distance between the locus of laser excitation and the lower extremity of the discharge.

A portion of the spectrum obtained by monitoring the fast signal under low resolution while scanning the laser frequency is reproduced in Fig. 29. By introducing an intracavity etalon, high-resolution measurements were executed and, by confining the spectral region scanned to the vicinity of the calibration markers, wavelength measurements accurate to ~0.01 cm⁻¹ were obtained.

The results of high-resolution measurements indicate that most of the absorption originates from the \( ^3P_2 \) 5d states and terminates on the \( ^3P_2 \) nf states of neutral atomic iodine, I(I). Other atomic
FIGURE 29. Spectrum obtained by monitoring the fast (atomic) LOG signal in iodine vapor.
iodine transitions \( (3P_e)6p[1]1/2 \rightarrow (3F_e)6d[2]3/2, (3P_e)6s[1]3/2 \rightarrow (3F_e)6d[1]5/2, \) and \( (3P_e)6p[2]5/2, \) and \( (3P_e)6p[3]7/2 \rightarrow (3P_e)12s[2]1/2 \) have also been identified. These transitions are listed in Table 4, where they are compared with those reported by Minnhagen [92]. Some unidentified lines are observed near the calibration markers; these are not assigned.

A portion of the spectrum obtained by monitoring the slow signal while scanning the laser frequency is reproduced in Fig. 30. This spectrum is the familiar \( X^1\Sigma_g^+ \rightarrow B^3\Pi_0^+ \) transition of neutral \( I_2 \). As mentioned previously, spectra identical to Fig. 30 are obtained in a conventional photoacoustic cell using a microphone as sonic transducer. Thus, the RFLOG spectra obtained by monitoring the slow (molecular) signal are, in fact, photoacoustic spectra. Indeed, the RFLOG device is a superior sonic transducer at low pressure (See Chapter VI). The technique of recording photoacoustic spectra with an RFLOG device (i.e., PARFLOG), has the additional advantage of being contactless, and may be used to study corrosive gases.

4. Discussion

The optogalvanic effect, as observed using pulsed laser excitation of an RF discharge, can be interpreted as follows. The discharge is sustained by collisional events which lead directly or indirectly to ion production. An example of such an event is associative ionization, which involves collision between an excited species and a neutral species, resulting in production of both an ion and an electron \( (A+A^* \rightarrow A_+^+e^-) \). A second example is electron
<table>
<thead>
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<th>Experimental</th>
<th>Minnhagen [92]</th>
<th>Assignment</th>
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</tbody>
</table>
FIGURE 30. Spectrum obtained by monitoring the slow (molecular) signal in iodine vapor.
Impact ionization, which involves collision between some ground state or excited species and a high energy electron and which results in the release of an ion and two electrons (\(A + e^- \rightarrow A^+ + 2e^-\)). The rate of these processes can be affected in two ways. First, laser excitation of an atomic species, which produces an electronically excited atom, promotes the ionization process because these species, which now lie close to the ionization limit, may be ionized by less energetic collisions. That is, state-specific ionization rates are deemed responsible for the optogalvanic effect in atomic systems. Second, overall ionization rates are affected by increasing the total kinetic energy of the system, thus increasing the average energy of the collisions. The increase in total kinetic energy can be accomplished by the degradation of vibrational to translational energy through V-T transfer, as well as by collisional deactivation of excited electronic states. In the case of iodine, dissociation of molecular iodine into two iodine atoms is likely to contribute to the kinetic effect, through a local pressure increase. (Such a dissociation is well known in I\(_2\), and is caused by a repulsive \(^1\Pi_u\) state that crosses the \(^3\Pi_0^+\) state of I\(_2\) at approximately \(v''=6\) lower state implied by double primes (\(v''\)). The time evolution of the optogalvanic signal is explicable on the basis of the above model. If sufficient numbers of electronically excited iodine atoms are created by the laser pulse, an immediate increase in the ionization rate should obtain. Hence, our identification of the fast signal as being atomic in origin follows.

The second mechanism, which involves degradation of energy
deposited by the laser pulse into kinetic energy (heat), takes a longer time to affect discharge kinetics. The energy must first be degraded by collisional events between slower moving molecular species and, finally, the pressure wave must propagate through the system. The latter process is limited by the speed of conduction of the pressure wave under the existing conditions of pressure/temperature in the discharge cell, and also by the distance between the locus of laser excitation and the discharge. Using 120 ms⁻¹ [90] for the speed of sound in iodine vapor at 25°C, it is estimated that the acoustic wave travels ≈2.4 cm in 200 μs, which is the value of the time delay of the molecular signal observed when directing the laser between the pick-up coil and the lower RF electrode, as shown in Fig. 4. A value of 2.4 cm allows the acoustic wave to reach a point about 1 cm above the lower RF electrode and, hence, to penetrate the lower region of the plasma. At that point, the pressure affects the discharge dynamics and produces a measurable optogalvanic effect.

5. Conclusion

A simple model based on collisional ionization rates for atomic and molecular species is sufficient to explain all experimental optogalvanic effect observations on iodine vapor in an RF discharge. The time evolution of the optogalvanic signal, as observed in time-resolved studies, is accounted for by assuming that collisional ionization rates depend on two factors: first, the degree of electronic excitation and second, the kinetic energy of the system.
as a whole. Rapid signals are produced in atomic systems because highly excited electronic states are easily ionized, even by low energy collisions. The slower signals observed for molecular species are due to a kinetic effect mediated by V-T transfer, by collisional deactivation of electronically excited iodine and by the dissociation $I_2 \rightarrow 2I$. These latter processes produce a pressure wave which propagates through the discharge cell at the speed of sound and which effects the discharge dynamics by increasing the average energy of collisions and, hence, the rate of collisional ionization.

Other observations, such as production of the optogalvanic effect by laser excitation of a region of the discharge cell far removed from the discharge itself, are also accounted for by this model. Finally, even the production of the optogalvanic effect by infrared photons in molecular systems is explained by the effects of V-T transfer in inelastic collisions on ionization rates.
CHAPTER VIII
CONCLUSIONS

A spectrometer designed to record laser optogalvanic spectra of low pressure gases in an electrical discharge has been constructed. The device employs the unique combination of pulsed dye laser excitation of a radiofrequency discharge, and signal recovery by means of an inductively coupled antenna to obtain high quality spectroscopic data. The device is particularly well suited to the study of highly energetic states of gaseous atoms and small molecules which are populated by the radiofrequency discharge.

The spectroscopic utility of the RFLOG spectrometer has been demonstrated in experiments on xenon, cesium, and nitrogen. By directing the laser into a discharge in low pressure xenon, several new Rydberg series have been observed which, despite much effort, have not been observed previously. In experiments on atomic cesium, results comparable in quality to earlier LOG studies were obtained. Finally, an RFLOG study of nitrogen was conducted, in which a rotational analysis of the nitrogen First Positive System was performed. The results were discussed in detail, and it has been shown that the RFLOG method is comparable to absorption and emission techniques in the study of electronic spectra.

In addition to functioning as a LOG spectrometer, it has been demonstrated that the RFLOG device functions as a sensitive transducer of the photoacoustic signal as well. By directing the laser beam into a region of the discharge tube some distance below the discharge itself, absorption by ground state molecular iodine
and subsequent relaxation give rise to a photocoustic signal which causes a mechanical perturbation of the discharge, and results in a LOG signal. The technique called PARFLOG has been successfully applied to a study of magnetic-field-induced level crossings in molecular iodine.

Finally, capitalizing on the advantage of pulsed laser excitation, time resolved measurements of the relaxation of the RF discharge in I$_2$ vapors subsequent to laser excitation have been performed. It has been shown that the signal due to absorption by atomic species is very rapid, whereas the signal due to absorption by molecular species is delayed in time. These results are important with respect to an interpretation of the mechanisms involved in the production of the optogalvanic signal in atomic and molecular systems.
1. F. M. Penning, Physica 8, 137 (1928).
11. C. R. Webster, C. T. Rettner and R. N. Zare, unpublished.


73. D. Cerny, F. Roux, C. Effantin, J. D'Incan and J. Verges, J. Mol. Spectrosc. 81, 216 (1980). These authors, under conditions which should have facilitated observations, were unable to detect the P\(_{13}\), Q\(_{13}\) and R\(_{13}\) branches.


77. See, for example, "Third International Topical Meeting on Photoacoustic and Photochemical Spectroscopy", J. de Phys. (Colloq, C6), (1983).


VITA

Phillip Lamar Clancy was born on February 27, 1952 in Shreveport, Louisiana. He graduated from Fair Park High School in May of 1970. Mr. Clancy received his Bachelor of Science degree in Microbiology in 1974 from LSU in Baton Rouge, Louisiana. He received his Master of Science degree in Microbiology, with a minor in Biochemistry, from LSU in 1978.

During the period 1979-1982, Mr. Clancy was employed by Kennon Environmental Services as an operator/technician, and by the Harry D. Wilson Feed and Fertilizer Laboratories as an analytical chemist. While working, he took university courses in mathematics and computer science on a part-time basis.

In January, 1983, Mr. Clancy enrolled as a full-time graduate student in Chemistry at LSU. He joined the Molecular Spectroscopy Group in 1984. Mr. Clancy is presently a candidate for the Ph.D. degree in Physical Chemistry.
Candidate: Phillip L. Clancy

Major Field: Physical Chemistry

Title of Dissertation: "Laser Optogalvanic and Photoacoustic Studies of Some Atoms and Small Molecules"

Approved:

[Signatures]

Major Professor and Chairman
Dean of the Graduate School

EXAMINING COMMITTEE:

Robert J. Gale
Robert V. Nauman
Michael L. Johnson
Mark J. McLaughlin
Paul Aharon

Date of Examination:

November 25, 1986