DIODE LASER DIAGNOSTICS OF LASER-INDUCED PLASMAS AND ATOMIC VAPOR CELLS

By

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A ma famille et mes amis,
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DIODE LASER DIAGNOSTICS OF LASER-INDUCED PLASMAS AND ATOMIC VAPOR CELLS

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Chair: James D. Winefordner
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The main goal of the research is focused on the exploitation of diode lasers for several applications involving photon detection, high resolution spectroscopy and imaging of selected species in laser induced plasmas. Laser Induced Breakdown Spectroscopy (LIBS) is commanding much attention as an atomic emission spectroscopy technique due to its multiple attractive features. Much effort in the LIBS community has been, and still is directed toward the understanding of plasma fundamentals. Understandably, much information remains to be gathered in order to fully comprehend the laser-sample interaction. Of all the diagnostic techniques applied to plasmas and extensively described in the literature, absorption spectroscopy seems to be receiving comparatively less attention. In this work, we describe the use of selective absorption methods to follow the evolution of the plasma in time, and as a consequence, to better understand the temporal and spatial evolution of the different populations involved. The temporal behavior of a specific transition can be followed by measurements with a Photomultiplier Tube (PMT) and line shapes can be evaluated by scanning the diode laser. In spectrochemical analysis, line shapes plays a major role in the understanding of spectral interferences, plasma conditions and behavior of analytical applications. By spatially expanding the laser probe beam, the temporal and spatial evolution can be followed with a gated Intensified
Charge-Coupled Device (ICCD), consequently assessing the studied species’ homogeneity within the plasma plume.

Cesium atomic vapor filters or detectors have been a primary focus of this work as they demonstrate the potential to excel both in terms of spectral resolution and sensitivity. Atomic vapor detectors have a spectral resolution that is governed by the properties of the atomic vapor used as the sensing element, while maintaining the same value of the luminosity. Cesium vapor cells have been extensively investigated because of cesium’s high number density at low temperature and its strong resonance transition in the near-infrared at 852nm ($6^2S_{1/2} \rightarrow 6^2P_{3/2}$). A promising fluorescence scheme for cesium has been demonstrated here that includes a single transition at 852nm and fluorescence detection at 894nm ($6^2P_{1/2} \rightarrow 6^2S_{1/2}$). For efficient detection, a rapid fine-structure mixing ($6^2P_{3/2} \leftrightarrow 6^2P_{1/2}$) is required and is provided by the presence of ethane in the cell. The absorption properties of this cell are reported as well as its potential application to a selected analytical problem such as the detection of Raman photons.
CHAPTER 1
INTENT AND SCOPE OF STUDY

The main goal of the research is focused on the exploitation of diode lasers for several applications involving photon detection, high resolution spectroscopy and imaging of selected species in laser induced plasmas. Laser Induced Breakdown Spectroscopy (LIBS) is commanding much attention as an atomic emission spectroscopy technique due to its multiple attractive features. Much effort in the LIBS community has been, and still is directed toward the understanding of plasma fundamentals. Understandably, much information remains to be gathered in order to fully comprehend the laser-sample interaction. Of all the diagnostic techniques applied to plasmas and extensively described in the literature, absorption spectroscopy seems to be receiving comparatively less attention. In this work, we describe the use of selective absorption methods to follow the evolution of the plasma in time, and as a consequence, to better understand the temporal and spatial evolution of the different populations involved. The temporal behavior of a specific transition can be followed by measurements with a Photomultiplier Tube (PMT) and line shapes can be evaluated by scanning the diode laser. In spectrochemical analysis, line shapes plays a major role in the understanding of spectral interferences, plasma conditions and behavior of analytical applications. By spatially expanding the laser probe beam, the temporal and spatial evolution can be followed with a gated Intensified Charge-Coupled Device (ICCD), consequently assessing the studied species’ homogeneity within the plasma plume.

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**Diode Laser Spectroscopy:** Semiconductor lasers or diode lasers have proven to be valuable tools in atomic spectroscopy. The active medium is a $pn$ semiconductor material, doped by a huge concentration of donors and acceptors, thus the Fermi level is in the valence band of the $p$ region and in the conduction band for the $n$ region. The population inversion, for laser action, is achieved by applying a voltage difference at the direct polarized junction. As in other lasers, the gain region is surrounded with an optical cavity to form a laser. The two ends of the crystal are cleaved to form perfectly smooth, parallel edges, forming a Fabry-Perot resonator.

Because of their electrical efficiency, low cost diode lasers provide the spectroscopic advantages of laser diagnostic in a compact, transportable and easy-to-use system. Compared to gas lasers, no external pumping is needed which significantly reduces the size and cost. A diode laser head can be smaller than a one millimeter cube; the laser reaches few centimeters dimension with an external cavity configuration. The temperature controller and power supply unit defines, the actual size of the entire laser device.
Such sources, in certain conditions, allow for single mode operation and a continuous single mode tuning range. Diode lasers are tunable source mostly for the infrared and red region of the spectrum, different wavelength regions are achievable by changing the semiconductor crystal. With the continuous development of laser technology, the emitted wavelength of diode lasers is now available in the blue region of the spectra. However, they are currently quite expensive compared to other diode lasers. Figure 1-1 shows all the elements as of 2005 that can be studied by applying the fundamental and second harmonic wavelengths of diode laser. Thirty five elements are directly accessible, nineteen by second harmonic generation.

The wavelength emitted by a single diode laser can be slightly tuned by changing the temperature and the supply current of the semiconductor. If the diode laser is working in multi modal operation, an External Cavity configuration can be used to force the laser to oscillate in a single longitudinal mode. Diode lasers with linewidth in the order of MHz are commonly achieved. In the Littrow configuration, the light emitted by a diode laser is directed to a tuneable grating as displayed on Figure 1-2. The 0th diffraction order is coupled out as laser beam and the 1st order diffraction is coupled back into the laser diode chip. If the feedback of the gratings is much larger than the feedback of the frontal edge of the laser, an optical cavity is formed between the back edge of the laser and the tuneable grating. In this case, the wavelength varies also by modulating the voltage applied to the piezoelectric element which rotates the grating of the external cavity. Other configurations exist commercially and a Littman/Metcalf configuration can be found on Figure 1-2. External cavity diode lasers features like narrow linewidth (<5 MHz), high passive stability (long term drift, typically of 300 MHz), fine and accurate tuning ability, are required for high resolution spectroscopy and have been commonly used for sub-Doppler spectroscopy. In atomic spectroscopy, the diode laser bandwidths are often narrower
than line profiles, specifically in laser-induced plasmas and therefore peak absorption measurements are possible. Because diode lasers are used in continuous wave mode, transient events in the plasma such as the absorption of a specific population can be continuously observed. Time-dependent detectors, photomultiplier tubes (PMT), photodiodes or Intensified Couple Charged Devices (ICCD) record the temporal evolution.

Several restrictions apply when using diode lasers for spectroscopic measurements. The coarse tuning range for those diode lasers are typically from 10 nm to 100 nm but a fine tuning, modehop free, is only possible over a maximum of 100 GHz (0.24 nm at 850 nm) and more often over a range of about 20 GHz. Therefore, those diode lasers have to be used for scanning over profiles with full width half maxima narrower than approximately 20 pm at 850 nm. The output power is often in the order of tens of miliwatts, even if higher powers are achievable, which limits the type of application. In atomic absorption spectroscopy, where low fluences are usually used to avoid saturating transitions, the power of those lasers is sufficient. External measurements with high spectral resolution are required to accurately monitor the output wavelength of diode lasers which can significantly complicate one’s setup. Fabry-Perot interferometric techniques are often used for wavelength calibration.
Figure 1-1. Elements that can be determined by applying the fundamental or second harmonic wavelengths of laser diodes. Elements in purple boxes can be measured from the ground state or low-excited state, elements in yellow must be measured from highly excited metastable levels in a plasma source. Appropriate diodes are not commercially available for the elements in white boxes.¹
Figure 1-2. External cavity diode lasers. Diagram, a), and picture, b), of an external cavity diode laser in Littrow configuration. Schematic, c), and picture of an external cavity diode laser in Littman/Metcalf configuration.²
CHAPTER 2
INTRODUCTION TO LASER INDUCED PLASMA SPECTROSCOPY

History and Fundamentals

Since the first report of laser operation in a ruby crystal in 1960, researchers have not ceased to ponder the mysteries of laser-light and matter interaction. With the development of Q-switched lasers, Brech and Cross, in 1962, demonstrated the capability to produce high focused laser fluences sufficient to initiate a breakdown and to produce an analytical plasma from solid materials. In 1963, Debras-Guedon and Liodec reported the analytical use of laser-induced plasmas for the spectrochemical analysis of surfaces, and in 1964, Maker, Tehrune, and Savage reported the first optical breakdown in a gas.

Over the years, this technique has been extensively reviewed in the literature. Several names and acronyms have been applied to Laser-Induced Plasma Spectroscopy (LIPS). These include Laser-Induced Breakdown spectroscopy (LIBS), Laser Ablation Optical Emission Spectroscopy (LA-OES), Laser Spark Spectroscopy (LASS). Laser-Induced Plasmas (LIPs) can be defined by the generation of a vaporizing and exciting plasma from a high energy density focused laser pulse. A glow or flash is generally observed in the focal region. One major characteristic of a LIP is its transient nature—the plasma evolves extensively both in space and time. Much effort has been made and has to be made in understanding the fundamental mechanisms governing LIP. The laser-material interaction leading to the breakdown is composed of two steps. The first involves absorption of the radiation, creating free electrons through three body collisions of electrons, photons and neutrals. The second step is avalanche ionization. The high velocity of the free electrons induces an increase in the thermal energy density that causes the underlying materials to reach critical temperatures and pressures and then explode. The materials from the explosion contain a high number density of electrons, ionized species from
collisions, and atoms that expand at supersonic speeds. A shockwave with the surrounding atmosphere is formed and is responsible for the loud sound usually associated with LIBS. A general feature of the interaction between the vapor plasma and the ambient gas is shown on Figure 2-1. After some time, several microseconds, the plasma plume slows down and cools. Due to radiative processes, quenching and recombination, a dense neutral region forms. A temporal evolution with the dominant emitting species during the plasma evolution is clearly summarized on Figure 2-2.6

Several factors have significant influence on the plasma characteristics. The behavior of the plasma is mainly dictated by the ablation laser, which supplies the required fluence to reach a breakdown. The type of laser, wavelength, pulse characteristics and beam quality, have different effects on plasma formation as does the focusing element and its position relative to the target.

**Laser Properties Used in LIP**

Almost all available types of pulsed-laser have been used as an excitation source for LIBS, from gas lasers to solid state lasers. The most popular lasers to create the breakdown are solid-state lasers and especially, lasers with an amplification medium doped with neodymium (Nd): Nd-YAG (yttrium-aluminum-garnet), Nd-YLF (yttrium-lithium-fluoride), Nd-YVO₄ (yttrium-orthovanadate) for instance. Nowadays, solid state Nd-YAG lasers (1064 nm) are the most commonly used in LIP studies and applications, and are generally equipped with an active Q-Switched and a flashlamp pump. Despite their higher cost, the number of diode-pumped lasers is continuously increasing due to their compactness and better shot-to-shot reproducibility. The fundamental wavelength can easily be converted to shorter wavelengths (532 nm, 256 nm and 355 nm) with harmonic generation crystals.
Other noteworthy types of laser are the CO$_2$ laser (10.6µm) and excimer lasers (XeCl, 308 nm, KrF, 248 nm, ArF, 193 nm). Several publications can be found using these lasers; however, gas lasers require high maintenance and are generally bulky and expensive.

**Laser Wavelength**

The laser wavelength-matter interaction has a direct influence on the plasma generation, it has been used as an advantage in terms of increased energy coupling with a particular sample. UV laser-induced breakdown leads, generally, to higher ablation efficiency, lower fractionation and background emission, but requires a higher fluence threshold and is associated with greater matrix effects. Several papers directly compared the effect of laser wavelengths on specific samples. The ArF laser and KrF laser were compared while removing coatings from historical objects. Within the same conditions, it was concluded that the ArF gives better results due to a specific absorption from the coating at the laser wavelength 248 nm. The different harmonics of a Nd-YAG laser were studied by Pinnick et al. on different aerosols and Costela et al. on spray paints. A higher spatial resolution can also be reached by UV lasers, an advantage that can be exploited for surface mapping in microanalysis.

**Laser Pulse Width and Energy**

One can easily understand that the pulse energy, as well as the fluence, affects directly the plasma evolution. Pulses with high energy result in larger and more energetic plasmas. Temperature, ionization, mass ablated from the surface and emission intensity; parameters conventionally used to describe a plasma are all increasing with the pulse energy.

The laser pulse width also influences the plasma formation and its properties. Conventional LIBS has mainly focused on several nanoseconds (ns) to tens of nanoseconds pulse widths, though a more recent interest in picosecond (ps) and femtosecond (fs) has grown. The ablation process and the morphology of the craters have been studied for those regimes. On the
femtosecond time scale, the mechanisms leading to plasma formation are dominated by multi-photon ionization over thermal processes. This results, compared to ns scale lasers, in higher ablation efficiencies. The material is removed without any thermal effect or melting beyond the ablated region. The temperature of the plasma also decays at a faster rate. The result is the decrease of background emission from the plasma and more specifically the continuum emission. A shorter plasma lifetime and a better resolution of spectral lines were also observed.

Despite some appealing advantages, the cost, complexity and power demand of femtosecond lasers are high and limit its use to a small scientific community. An alternative approach to improve analytical figures of merit that have received significant interest is the use of dual- or multiple laser pulses. In a double-pulse experiment, a second laser is applied after a certain delay from the first one. Several delay times and geometry configurations (orthogonal or parallel, for instance) have been reported. Although the mechanisms behind the improved figures of merits are not completely clear, there is an agreement in the possible sources of enhancements, higher ablated mass, re-excitation of the material ablated in the first pulse and energetic and physical effects from the first pulse.

**LIBS Setup**

The common LIBS setup records the emission intensity of atomic and ionic lines versus the wavelength during the entire plasma lifetime. Figure 2-3 shows the diagram of a generalized LIBS instrument. It includes a pulsed laser, a method of spectrally selecting one or more narrow regions of the emission lines and a detector. Several factors are taken into consideration when choosing the components for the apparatus: the elements to be monitored (wavelength, number of elements), the nature of the sample and the type of analysis (quantitative or qualitative). Those factors will influence the collection elements (lenses or fiber optics), the nature of the
spectrometer (Echelle spectrometer, Czerny-Turner type monochromator) and the detector (Photomultiplier tube, CCD, gated-CCD, ICCD, photodiode). For instance, the price for high spectral resolution is a higher cost and narrow spectral window. Depending on the number of lines desired, the window should be carefully chosen. Niemax et al. reported the use of an Echelle spectrometer coupled with an ICCD. They improved the precision and detection limits by observing multiple lines from single laser shots. Time-resolved LIBS is used to determine the time-evolution of line intensities emitted from different species. Baudelet et al. presented the characteristics of the spectra obtained from organic species and particularly molecular species such as CN, which exists at longer delay time and result from recombination. Gated detectors are commonly used to eliminate the continuum background emission at early times.

Other parameters or conditions that greatly affect the plasma evolution have been studied, including temperature, pressure, buffer gas and the matrix composition of the sample.

**Applications of LIBS**

Hundreds of potential and actual applications for laser induced plasmas can be found in the literature. Presenting an extensive overview is not the scope of this work. However, several applications which take advantage of the simplicity, remote capabilities and low-destructive properties of LIBS are worth noting.

Laser ablation is an attractive tool for alloy and metallurgic industries because samples can be analyzed without pretreatment. On the industrial scale, this saving of cost and time is of primary importance and several of efforts have been resulted in the implementation of LIBS. LIBS has been used to monitor industrial processes, especially in the steel industry. Brass, gold and aluminum alloys have also been studied. Some examples involve microanalysis of surfaces such as the detection of defects and elemental analysis, the analysis of molten alloys with high temperature resistance probes and the analysis of scrap metals in industrial applications.
for sample quality processing. Other industrial applications of laser ablation include welding, cutting and micromachining.

Another interest in using LIBS is attributed to its potential *in-situ* field analysis, notably in environmental analyses. The reports of “portable” LIBS devices have increased over the years with the constant miniaturization of lasers, spectrometers and computers. Research has been done in and outside the laboratory on organic materials like plants, wood, soil. Capitelli et al. evaluated the performance of quantitative and qualitative analyses of heavy metals in soils. The performance of using LIBS was compared with Inductively Coupled Plasma (ICP) emission analysis. As generally found in the literature, lower limits of detection were found with ICP based techniques, mainly when coupled with a mass spectrometric detector. However, ICP methods usually require digestion procedures and are not portable. Cremers et al. measured total soil carbon by placing the sample in a small quartz tube. LIBS measurements give satisfactory results when compared with measurements obtained using the conventional dry combustion method.

Other biological matrixes like blood, hair and bacterial spores and samples including pharmaceuticals, plastics, oil and ceramic products have been investigated. The main problem faced by those who want to employ LIBS with complex samples is in the interference caused by matrix effects. Several methods can be used for improvements like internal standards or other calibration methods. One interesting approach is calibration-free LIBS which overcomes the matrix effect without the use of calibration curves. Statistical methods can also be used to improve the interpretation of spectroscopic data. Nowadays, more people are combining LIBS with chemometrics, such as partial least-squares regression, pattern recognition (principal component analysis and cluster analysis) and neural network analysis.
The depth profiling ability of LIBS is another advantage for different applications. By recording the distinctive plasma emission from successive single laser shots on the same spot, the local composition of the material at a particular depth can be studied. This approach has proven useful for investigating inhomogeneous or multi-layer samples, as reported by Anderson et al. using zinc coated steel.57

Some fields are in need of non-(or minimally) destructive techniques. This is the case in the conversation and restoration of cultural inheritance in art and archeology. LIBS have been used to determine the chemical composition of paints58 and more precisely the identification of different pigments and additives in paintings to enable a better restoration or for testing their authenticity.59

Remote-LIBS can be used when the analysis requires large distances from the target. Lopez-Moreno et al. 60 demonstrated stand-off detection of rocks, soil and vegetation with the use of a telescope at a distance greater than 10 m.

Conclusions

LIBS has found several niches. Its simplicity for elemental analysis allow to this technique to achieve acceptable results over a large range of applications. In combination with other techniques, more particularly molecular techniques such as Raman spectroscopy, the range of applications of LIBS are likely to increase.
Figure 2-1. Different plasma features within the shockwave.
Figure 2-2. Important time periods after plasma formation during which emissions from different species predominate. The box in a) represents the time which the plasma light is monitored using a gatable detector. Time-resolved plasma emission detected with a photomultiplier tube (PMT) at a spectral window containing an ionic and atomic line, b).
Figure 2-3. General laboratory bench-top setup for Laser Induced Breakdown Spectroscopy
CHAPTER 3
RESONANT ABSORPTION IMAGING IN LASER-INDUCED PLASMAS

Introduction

Over the years, a continuous effort has been and is still directed toward the understanding of the laser-sample interaction and plasma evolution. Understandably, much information can still be gathered to fully comprehend laser ablation processes. Different complementary diagnostic techniques have helped to improve the analytical performance of laser-induced plasmas. Several theoretical models have been developed to fully describe the evolution of different species, as well as the major plasma parameters: temperatures, electron number densities, broadening parameters, velocities, etc.

Laser-aided diagnostic methods are used extensively in a wide variety of fields in almost all areas of science. Laser spectroscopic methods are often characterized by high resolution and accuracy and have several advantages for plasma diagnostics. Tunable lasers can provide spectral information and high spatial and temporal resolution can be achieved from lasers beam properties, such as beam size and coherence. Another key element is the possibility of imaging with the help of a beam expander and a two dimensional detector. In addition, the laser source and the detector can be located far from the object to allow measurements in a the presence of a high luminosity background. Optical diagnostic techniques are, in general, non-intrusive, allowing the study of non-perturbed plasmas. For this reason, they are invaluable components in experimental plasma studies.

Of all the diagnostic techniques applied to plasmas (ICP, microwave…) and extensively described in the literature, laser absorption spectroscopy seems to be the one having received comparatively less attention. This maybe due to the fact that the laser plasma is highly luminous and therefore a high intensity radiation source is necessary in order to overcome the
strong background continuum which limits the attainable signal signal-to-noise ratio. Diagnostics techniques include laser-induced fluorescence, emission spectroscopy, shadowgraphy imaging, laser-enhanced ionization, X-ray spectroscopy and scattering processes. From an analytical point of view, absorption spectroscopy has the advantage over the other techniques (emission and fluorescence) that it is easily amenable to quantification. In other words, an absorption scan over the line profile or a peak absorption measurement can directly provide the total number density of absorbing species, if the oscillator strength of the transition is known.\textsuperscript{70}

Another advantageous feature of the absorption technique would be the possibility of measuring absorption line profiles and therefore gain a better insight on the main broadening mechanisms operating in the plasma. This will be possible if a narrow excitation source, such as a diode laser, can be frequency scanned across the profile.

Lastly, if a very narrow laser beam is directed into the plasma, vertical line of sight measurements can be obtained with the corresponding spatial distribution of the absorbing species. Alternatively, the laser beam can be made larger than the plasma and one can there obtain spatially resolved distribution of the species with the use of a bidimensional detector (CCD).

This chapter will focus on the use of diode laser absorption spectroscopy to obtain information about the plasma morphology and its relation to laser-induced plasma analysis. Spectral considerations are the focus of the following chapter.

**Resonant-Absorption Imaging for Morphology Studies:** The plasma morphology or spatial structure of the plasma produced by laser pulses provides valuable information on the distribution of atomic species in the plasma and their dynamics. Morphological data can be applied to understand and to improve LIP analytical figures of merit in several ways. Signal
fluctuations in LIBS analysis has been a major problem, especially laser shot to shot instability, variation of the sample surface and the non-linear dependence of several plasma parameters. Integrating the signal in a LIP over several laser shots can, then lead to rather poor results. On the other hand, morphological information from a single laser-shot can be used for proper analysis of spectra or for selecting the part of the plasma characterized by the best analytical results. Xu et al. 71 used such data to re-normalize their emission spectra according to the conditions of specific plasmas. The renormalization approach has also been used in aerosol analysis to compensate for individual variations. 72 Plasma morphology can also be used to find the best sampling conditions by optimizing optical geometry. 73

Most of the techniques used to study the morphology of a LIP can be found in the literature of inductively-coupled, microwave, glow-discharged and arc plasmas.

Perhaps the most widely used method for obtaining spectral information from various locations in the plasma is spectrometer slit imaging. 74, 75 Simultaneous two-dimensional information can be achieved by using an imaging spectrometer (a lens and a monochromator) and a CCD camera. However, for each individual plasma formation, the spatial vertical dimension is limited by the direction along the slit and a translation of the plasma is required to obtain the full image of the plasma. With a CCD coupled with an intensifier, time-resolved images are produced by a proper gating of the high voltage applied to the microchannel plate. If an interference filter is placed in front of the CCD detector, minimal spectral resolution of the plasma images can be obtained. A tunable filter offers the advantage of allowing easy spectral acquisition. The tunable filter may be of the liquid crystal type 76 or of the acousto-optic type 40. In both cases, however, a limited spectral resolution is obtained, ~5 nm for liquid crystals and few nanometers for acousto-optic filters. Over such a “wide” spectral window, several lines,
atomic or ionic, are likely to be present, making it difficult to observe the population of single selected levels.

Another approach to spectral imaging is to use spectrally resolved sources. Previous absorption measurements in ICP plasmas have attempted to use modulated electrodeless discharge and glow discharge lamps as spectral sources. The radiation of these lamps is usually not intense enough to overcome the luminosity of the plasma, especially at earlier delay times when the continuum is still present. Absorption measurements using fixed-frequency sources provide a measure of absorbance for a narrow spectral region under a line profile and cannot be used to determine the overall absorption feature.

Near-resonance or resonance absorption and shadow imaging is another tool widely used for plasma morphology. In most cases, the plasma plume is created and the absorption measurement is obtained by recording the transmitted light of a secondary pulsed laser. The beam is enlarged and spatially filtered to illuminate as uniformly as possible the plasma over its whole extent. The high directionality of the beam over long distances allows line-of-sight absorption measurements in highly luminous plasma environments. The plasma images in Figure 3-1, obtained by absorption shadowgraphy show two distinct features: a white, dark-fringed line external to the laser spark body, which is produced by the refraction of the laser light at the shock-wave propagating in the medium, and dark areas which are produced by absorption of laser light by the ionized gas. If a tunable laser is used as the excitation source, resonance shadowgraph images can be related to single species in the plasma. Among the many possible techniques available to observe the morphological properties of the plasma, the resonant absorption imaging with a tunable diode laser developed in this work combines many interesting features. Resonant absorption imaging offers the possibility of following the temporal evolution
of the morphology of an individual population in a single laser shot with the inherent spectral advantages of diode lasers.

Atomic and ionic species have been thoroughly studied in the literature but little attention has been paid to the ground state population of atoms. Whereas the most common diagnostic approach, emission spectroscopy, is normally unable to give direct information about the ground state population, absorption spectroscopy provides complementary measurement and will further improve our understanding of the processes of plasma creation and evolution. Due to the availability of diode lasers at wavelengths of the ground state atomic population of cesium, cesium plasmas have been investigated in this work.

**Experimental**

**Experimental Setup**

A detail schematic of the experimental setup for resonant absorption imaging of ground state cesium is shown in Figure 3-2. The excitation laser source used to generate the breakdown is a Q-Switched Big Sky Ultra Nd-YAG laser with maximum pulse energy of 50 mJ, though a power of 25 mJ is used in all experiments. The laser produced 9 ns pulses at the fundamental wavelength of 1064 nm and is fired at a repetition rate of 1 Hz. If not mentioned specifically, the pulse is focused slightly below the sample surface, at distance of 0.2 inches from the focal plane of the lens. The focal length is 2 inches. The sample is placed in a vacuum chamber pumped by a mechanical pump and controlled by a needle valve to allow a range of pressures from ambient pressure, 1 bar to 0.01 mbar. The chamber is made of brass and has multiple accessible windows for line-of-sight measurements in the plasma. The chamber is placed on an XYZ stage to adjust for difference of heights between samples and to assure fresh ablation areas for successive laser shots.
The probe radiation at 852.34 nm, corresponding to the D\textsubscript{2} ground state \(6S\frac{1}{2} \rightarrow 6P\frac{3}{2}\) transition of atomic cesium, is provided by an external cavity diode laser operated in Littman-Metcalf configuration (Model TEC 500, Sacher Lasertechnik, Marburg, Germany) with a manufacturer specified linewidth of 5 MHz. It is a safe assumption that such linewidth is much narrower than the absorption line in the plasma. An iris is used to restrict the radiation diameter to 1mm, providing a homogeneous radial intensity distribution. The probe beam is then expanded by a beam expander, which consists of a short focal length diverging lens followed by a converging lens. The distance between the two lenses is adjusted to provide a well collimated beam of several centimeters in diameter. The size of the beam exceeds the plasma dimensions to ensure a full illumination of the entire plasma volume.

A small fraction of the beam is sent through a low pressure cylindrical cesium sealed cell (Opthos Instruments, Inc., Rockville, Maryland) and detected by a near-infrared photomultiplier tube (R636, Hamamatsu, Japan). The PMT output is amplified (Model 427, Keithley Instruments, Cleveland, OH) and recorded by an oscilloscope (TDS3000 Series, Tektronix, Willsonville, OR). This fraction of the beam permits tuning the diode laser to the center of the strong hyperfine component of the ground state transition \(F=4\). This assures that all measurements are done at the peak absorption and that no mode hopping occurs; the laser emits in the single mode configuration.

Resonance radiation transmitted through the plasma is directed into an 852 nm interference filter (Optometrics, LLC, Ayer, MA) to spectrally eliminate background light and protect the detector. The detector is placed several feet away from the sample to further minimize the isotropic continuum emission, present at early delay times, that could saturate the detector. The detector is a Princeton Instrument (PI Model# ICCD-576S) gated 2-D Intensified Charge-
Coupled Device (ICCD). The ICCD photosensitive face or photocathode contains a grid, 576 x 384, of 2.2 µm pixels. Incident photons striking the photocathode release electrons that are then accelerated towards a micro-channel plate (MCP). A fluorescent screen absorbs the amplified electrical signal and the photons emitted are detected by a CCD. A schematic of the ICCD detector is shown in Figure 3-3. Different exposure times with different delays can be achieved by controlling the gate voltage between the photocathode and MCP. The gate is adjusted from the PG-200 (Princeton Instruments) pulse generator and triggered with the output Q-Switch of the Nd-YAG laser. A signal from the pulse generator is sent to the ST-138 camera controller that synchronizes the CCD with the gate and sends the output image to the computer.

**Sample Preparation**

For this study, two different types of sample have been prepared. Cesium pellets in a cellulose matrix are prepared by soaking a known amount of cellulose into a solution of known concentration of CsCl. The mixture is then dried overnight and carefully ball-milled before being pressed at a specific pressure to form a homogeneous pellet. The final concentration of the pellet can then be calculated, assuming that all the water has been evaporated and that the CsCl has been retained by the cellulose matrix. Different pellet concentrations can easily be achieved by changing the solution concentration and a 10 ppm pellet was chosen for the following study. The last pellet provided a number density of cesium in the plasma which resulted in a transmittance of the order of 50%. In absorption, the concentration of the analyte is based upon the difference between two large signals: the detector signal in the presence and absence of the analyte, which, in this case, is synonymous with detecting the signal on and off resonance, respectively. However, a CCD detector is known to have a limited dynamic range, lower concentrations resulted in a very weak absorption and higher concentrations resulted in such strong absorption that the study of the morphology of the plasma becomes difficult. Suitable contrast in the images
was not obtained with transmittance lower than a few percent. A second type of sample was provided (courtesy of Dr. Galan Moore from Corning Inc). CsCl fused pellets were prepared using standard additions. The CsCl and the Li$_2$B$_4$O$_7$ flux were added together and ball-milled. SiO$_2$ is then added and the standard is ball-milled again. SiO$_2$ was added to the CsCl flux mix in order to make the pellets opaque for better absorption of 1064nm radiation. Several concentrations have been provided and a 0.1% of cesium pellet was chosen for this work.

Not only do the fused silica and cellulose pellets have a very different matrix in terms of chemical composition, but their roughness and rigidity also cause strong variation in mass removal. Cellulose pellets are similar to a fine powder that binds together while fused silica pellets are extremely rigid with a smooth and reflective surface. The microscope pictures of the laser craters after one and ten laser shots on the same sample spot can be seen in Figure 3-4. The obvious difference in crater diameters, approximately 500 µm in diameter for the cellulose pellet and 200 µm in diameter for the fused silica is easily explained by their rheology. The difference in mass ablated understandably results in disparate number densities of atomic cesium in the plasma plume. This explains the use of different concentrations, 10 ppm and 0.1%, with in the cellulose and the fused silica matrices, respectively, that provided suitable contrasts for the plasma morphology study.

**Data Acquisition**

All the ICCD images were captured and mathematically processed by the WinSpec32 software v2.5.18.2 (Princeton Instruments, NJ). Monochromatic radiation traversing several optical surfaces such as lenses and filters creates interference patterns due to etalon effects. Those patterns, which are highly dependent on the laser beam direction and on the wavelength, are recorded by the detector as well as plasma absorption. Optical elements can also present some defects that will alter the perceived morphology of the ground state population. To correctly
account for these phenomena, a reference image had to be taken for each set of measurements or every time a parameter was changed. The reference image served as the true $I_0$. The plasma transmittance was then plotted using the well known relation

$$T = \frac{I - I_{\text{dark}}}{I_0 - I_{\text{dark}}}$$

(3-1)

where $I_{\text{dark}}$ is the dark image. The dark image was recorded when the MCP voltage was turned off. Figure 3-5 shows a typical absorption image, the reference image and the resulting transmittance image. The color scale represents the transmittance intensity. It is important to note that those images represent the overall transmittance of the plasma by species absorbing at the probe laser wavelength and not only by the cesium ground state population. For the particular image shown on Figure 3-5, the absorption by the shockwave can be observed from the concentric half circles. The “blue” circle represent values of transmittance lower than one while the “red” circle indicates values of transmittance higher than one: this result can be easily explained by the fact that the shockwave is deflecting a part of laser radiation, accounting for an apparent absorption. A similar halo can be observed around the “mushroom” shaped absorption because of the deflection of the beam caused by the change in index of refraction. To assess which portion of the plasma represents the cesium ground state absorption, images were taken with the laser tuned to the maximum absorption of the cesium transition and detuned by several tenths of nanometers. This is illustrated in Figure 3-6. Throughout the entire duration of the plasma, no transmittance lower than 70% is observed when the laser is tuned away from the transition, except for a very small layer close to the sample surface (i.e. at grazing incidence) and at the location of the shockwave. The lower values of the transmittance (darker scale on the images) are therefore only attributed to cesium ground state populations. A linear scale from 0 to 0.8 in transmittance is chosen for all the images from this work. The dimensions of the plasma
are calibrated with reference to a vision target that displayed precision test patterns printed on a glass substrate. The spacing between two lines of the dimension scale is displayed in every Figure and is always set to 1 mm.

**Results and Discussion**

**Time-resolved Atmospheric Plasma Evolution**

Time-resolved resonant images produced on cellulose pellets at atmospheric pressure are shown in Figure 3-7. The gate width was set to 0.5 µs and the delay varied from 1 µs to 150 µs. It should be noted that the transmittance values are independent of the laser probe energy. No differences were observed when neutral density filters attenuated the intensity of the radiation. Thus, all imaging experiments were performed under linear interaction between the laser and the atoms.

Several papers \(^7\), \(^8\)-\(^6\) have described time evolution of different species in the plasma plume and typical morphologies similar to those obtained here were reported. Once the electron number density of the vapor plume is greater than a critical number density, the vapor plume reaches a critical temperature and rapidly undergoes an almost one-dimensional expansion along a preferential axis, i.e., along the focusing lens axis. The rapidly expanding vapor further compresses the background gas as it expands, generating a strong external shockwave in the background gas region. For high background pressures, a blast wave model has been used to describe the shock front caused by the expansion of laser ablation plasmas.\(^8\)\(^7\) This model describes the propagation of a shock wave, caused by an explosive release of energy through a background gas and is applied to this work (cf. Figure 3-8). The propagation of the shock front by the background gas follows the laser supported detonation wave model and is described by the following distance-time relation
where \( n \) depends on the symmetry of the shock front (\( 1/4 \) for a cylindrical geometry). This model provides an approximate initial velocity of the shockwave, on the order of \( 10^5 \) m/s which is coherent with measurements from other works. After several microseconds, the speed of the external shockwave decays to a sound wave as the pressure of the shockwave approaches the background gas pressure.

The absorption of ground state cesium increases with time as the plasma temperature decreases, as the atoms recombine and the electrons decay to the ground state. At early delay times, most of the atomic population appears to occur at \( \sim 2 \) mm above the surface, where the front of the plasma core contracts. The compression from the background gas in the leading edge of the plume corresponds to a “snowplow” effect. The large velocity and temperature gradient between the vapor plume and both the sample and the background gases generates a boundary layer during expansion of the plume. This boundary layer is the source of vorticity in the flow of the plume and strong vortex rings provide strong velocities that lift the vapor plume. Additional outward velocity creates the “mushroom” shape, clearly observable for few microseconds and the plume changes to a more spherical shape at a 10 µs delay. The high absorbing region moves towards the sample surface tens of microseconds after the laser pulse terminates when the interaction with the background sufficiently reduces the strength of the vortex rings. Even after very long delay time, hundreds of microseconds, a strong absorption from the ground state is still clearly visible.

Figure 3-9 shows the same time-resolved plasma evolution for fused silica pellets. It is difficult to directly compare the transmittance values with the cellulose matrix, due to their distinctive nature, but the time evolution shows a similar behavior. Lower transmittances are
located in the plume front, lifted by ~2 mm from the surface during the first microseconds and
the population collapses towards the surface at later delays. Ground state cesium seems not to be
absorbing at early delay times in the region between the front of the plume and the surface. One
could speculate that higher laser energy is absorbed by the surface, resulting to a faster expansion
of the plume, generating a stronger vortex ring. The plasma would likely be more ionized,
consequently decreasing the absorption of the ground state atomic cesium outside the front
plume.

**Effect of the Pressure on the Plasma Evolution**

The ambient gas pressure influences in the plume morphology and has been studied by
several groups.\(^{82,92,93}\) Plume images obtained at different pressures for two delay times are
shown in Figure 3-10. The effect of the pressure on the plasma evolution can be described by
three pressure regimes. **Below 1 mbar**, the ambient gas pressure is such that the plasma expands
without collisions from the ambient gas molecules: as a consequence, no sharp boundary is
formed. The plume is expanding freely and the distribution of the cesium ground state is
associated with time-of-flight measurements. **For higher pressure**, the plasma becomes more
collisional. Narrowing of the plume is clearly visible as the pressure is increased. Note that at
pressures of 5 mbar and higher, a narrow stream of dense absorption is observed along the center
line of the plume, indicating a significant concentration of absorbers there. The gas molecules
have compressed the plume to form a symmetrical elliptical shape. The time-resolved absorption
at 5 mbar is presented in Figure 3-11. It has to be noted that the absorption reaches two apparent
maxima, around 0.3 µs and 2 µs. These two maxima will be discussed in more details in the next
chapter.

When the pressure is increased to 25 mbar and more, a compressed region is formed
between the expanding cesium plasma and ambient gas. Here the transition to a hydrodynamic
regime takes place, with the plume acting as a piston on the surrounding ambient environment.\textsuperscript{91} This compressed region moves ahead of the plume and generates a shock wave. It also leads to enhance absorption from the plume front as a result of transfer of plume kinetic energy into thermal energy plume heating. When a shock boundary is formed between the plume and ambient gas medium, it effectively shields the diffusion of the ambient gas species from the plasma species. A strong vorticity occurs, lifts the plume and diffuses the species radially.\textsuperscript{92}

**Effect of the Laser Focusing Distance**

The ground state distribution for different focusing distances at a few delay times for cellulose pellets at atmospheric pressure is presented in Figure 3-12. The focal length used in this work is 50.8 mm and the sample was positioned at different focusing distances below the sample surface. The position of the sample relative to the focal plane of the lens plays an important role in the analytical use of LIP and has been studied by several groups.\textsuperscript{94, 95} A significant variation is observed, both in the shape of the distribution and the transmittance values. When the laser is focused well below the surface, the absorbed irradiance by the surface decreases and a smaller plasma is observed. At an intermediate focusing distance, absorption and plasma stability are obtained and the shape assumes an increased spherical symmetry, which makes this distance the optimum when the plasma is used as an analytical spectroscopic tool. The optimum focusing is produced when the sample is placed at approximately 10\%, or 5 mm in this experiment, below the focal plane of the lens, where the laser irradiance corresponds to approximately 10 GW/cm\textsuperscript{2}. At focusing distances closer to the lens focal plane, the plasma becomes elongated along the lens axis. An extreme case results in the breakdown of the air above the sample. An air breakdown not only affects the plasma shape but also the plasma reproducibility, and needs to be avoided in analytical applications.
**Shot-to-shot Reproducibility**

Several parameters influence the LIBS measurement and account for the well-known relatively “poor” precision of the technique. Intrinsic noises, which can be shot noise, detector noise or instrumental noise do not account for all of the poor repeatability of LIBS. The plasma time evolution as described previously, dramatically affects the plasma spatial structure. As a consequence, the probed or collected region that produces reproducible analytical measurement has to be chosen carefully. For a specific delay time, the plasma morphology may also vary due to sample heterogeneities. Heterogeneities arise within disparities in the sample concentrations, surface profiles but also from the successive laser shots hitting the same crater. One of the most common approach to improve the precision of LIBS measurements is to accumulate several (n) shots to reduce the shot noise as $\sqrt{n}$ but the number of shots in the same crater is generally limited by modification of the sampled surfaces and formation of craters.\(^6\) Figure 3-13 shows the transmittance of successive laser shots on the same crater of the sample. A deeper and deeper crater is created after every shot, changing the focusing distance and the sample surface characteristics due to melting effect. For cellulose pellets, Figure 3-13 a), in which the ablation dimensions are greater, the ground state distribution and concentration varies significantly. The plume is extended along the lens axis as the number of shots increases and a considerable variation in the transmittance is observed. Fused silica pellets generate more reproducible plumes, as shown in Figure 3-13 b). The first shots are often, considered as “cleaning” or “preparatory” shots, as the laser interacts with a fresh and rough surface that can contain dust, an oxidation layer or other contaminants not representative of the sample. A significant difference in the morphology and a lower absorption is observed for the first shots. For quantitative measurements, the first few shots are often discarded to improve repeatability. The set of images from Figure 3-13 are a good example on how careful the LIBS user must be when performing
quantitative measurements; the plasma evolves in time and in space and the choice of the region and time-scale observed is essential. It can vary from sample-to-sample, cf. cellulose versus silica matrices, but it can also be a function of several other parameters that were not investigated here, such as laser energy and sample temperature. The average transmittance, binned from a 1 mm to 1 mm square centered in the shock front of the plume where the transmittance is minimal and where the best repeatability was found, is plotted in Figure 3-14 for two delay times. There is evidence of a drift in the transmittance, which is more pronounced with the cellulose pellets. This is likely due to laser heating and change in the focusing distance. As expected, an improvement in the relative standard deviation (RSD) is observed when the first two shots are not included. The experimental RSD of the transmittance found are of the order of 10%.

**Conclusions and Remarks**

Spatial and time evolution of the cesium ground state population in laser-induced plasma are studied for different pressures and for two significantly different samples, a powder bonded cellulose sample and a fused silica sample. The morphology of laser-induced plasmas is greatly affected by several parameters, namely the sample matrix, the focusing ablation laser and the shot-shot reproducibility. The plasma evolves rapidly in time and space and different pressure regimes drastically change this evolution. Imaging measurements with an ICCD reveal spatial variation within the plasma formation as well as its structure. By evaluating the plasma homogeneity, the area of the plume at different delay times where the best signal-to-noise ratio is obtained, can be determined. As a practical outcome, the knowledge of these different morphologies will help designing and implementing the optical collection and detection system in order to achieve the optimum analytical performance.

This chapter focused on two specific concentrations, according to the nature of the sample. These concentrations provided the best contrast images for structure studies. In terms of
analytical performance, these ICCD images would give poor figures of merit. The low dynamic range of the ICCD greatly limits the use of these absorption images for quantitative measurements. For concentrations ten times higher, the plasma is optically thick, resulting in two absorption regions, while for concentrations ten times lower, no absorption can be measured. It should be noted that different possibilities exist to improve the dynamic range. Several groups described an extended range of the detection with diode lasers by scanning the laser wavelength to the wings of the absorption profile. If the profile is mainly due to collisional broadening, especially at longer delay times, the absorption in the wings can be obtained at much higher concentrations of the absorbers while maintaining a linear relation with the concentration. However, an accurate knowledge of the absorption profile and the possibility of adjusting the diode laser to known frequencies is required to successfully improve the dynamic range.

As already said earlier, absorption measurements have been used in diagnostic measurement not only for morphology studies but also as direct measurement of plasma number densities. However, in this case, spectral information is required. The following chapter will focus on spectrally-resolved absorption spectra of the cesium ground state population.
Figure 3-1. Experimental setup used for shadowgraphic imaging of plasma evolution and the resulting images. Shadowgraphy of the laser-produced plasma and shock wave evolution is displayed on b). The photograph (right bottom) has a delay time of 375 ns with respect to the laser pulse, while the temporal delay between photographs is 500 ns. The shock wave position is highlighted with dashed semicircles.
Figure 3-2. Experimental setup for time-resolved laser-induced plasma absorption images at different pressure with a high resolution diode laser.
Figure 3-3. Schematic diagram of gated 2-D Intensified Charge-Coupled Device (ICCD)
Figure 3-4. Microscope images of the laser craters. Images are taken after a) c) one and b) d) ten laser shots at 25 mJ. The top images are taken from a powder-type sample, 10 ppm CsCl in a cellulose binder. The bottom images are taken from a fused silica pellet that contains 0.1% CsCl.
Figure 3-5. Absorption images at 852.4nm from laser-induced plasma on cesium based pellets. The transmitted signal, $I$, and the reference signal, $I_0$, combine to display a transmittance image, $T$ of all the species absorption at this wavelength. The scale of the transmittance image is shown at the bottom.
Figure 3-6. Diode laser images of laser-induced plasmas for the ground state resonance frequency of cesium. Images are shown on resonance on the left and for a wavelength detuned from the transition on the right. The color intensity represents the transmittance and the scale is shown on top.
Figure 3-7. Temporal evolution of the cesium ground state population. Images taken for single shots on 10 ppm CCl\textsubscript{3} cellulose pellets. The transmittance scale and dimension scale is displayed at the bottom.
Figure 3-8. Time propagation of the shockwave created from a LIP. Samples of 10 ppm CsCl cellulose sample were used. The evolution curve in red is fitted to a laser supported detonation wave model for cylindrical geometry.
Figure 3-9. Time evolution transmittance of the cesium resonance ground-state. Measurements are for 0.1% CsCl fused silica pellets at atmospheric pressure and single shots.
Figure 3-10. Cesium ground state absorption images for several pressures. Images taken at two delay times, a) 2 µs and b) 5 µs.
Figure 3-11. Time evolution transmittance of the cesium resonance ground-state. Images taken for 0.1% CsCl fused silica pellets at a pressure of 5mbar for single shots.
Figure 3-12. Effect of the focusing distant on the cesium ground state distribution for several delay times. The focusing values are the distances of the surface of the sample from the focal plane of the lens.
Figure 3-13. Successive LIP on the same target spot for two matrices. a) cellulose and b) fused silica.
RSD 7µs = 21%  (16% without shot 1&2)  
RSD 19µs = 9.3%  (8.7% without shot 1&2)  
RSD 5µs = 11%  (8% without shot 1&2)  
RSD 15µs = 11%  (8% without shot 1&2)

Figure 3-14. Transmittance values for successive laser shots on the same target spot. In a) cellulose matrices and in b) fused silica matrices were used. The relative standard deviations are given on the top of the graphics.
CHAPTER 4
HIGH-RESOLUTION TIME-RESOLVED ABSORPTION SPECTROSCOPY IN LASER-INDUCED PLASMA

Introduction

In the previous chapter, it was shown that spatially resolved absorption images of laser-induced plasma provided valuable information on the plasma spatial structure and the population distribution. Time-resolved morphology was measured using a gated detector, an intensified charge-coupled device (ICCD). Time evolution was discretely plotted for successive laser shots by changing the gate delay on the ICCD and therefore non-gated detectors with temporal discrimination are more suitable for time-resolved measurements. Photomultiplier tube (PMT) detection provided complementary measurements to spatial absorption images.

The shape of spectral lines in plasmas is a topic of strong interest and has been the subject of study for many years. In spectrochemical analysis, line shapes play a major role since it helps understanding spectral interferences, verifying plasma conditions (optically thin or thick) and explains the behavior of analytical calibration curves. The role of spectral line shapes as a diagnostic tool is magnified because of the abrupt spatial and temporal gradients which exist during the formation and evolution of a LIP. The derivation of atomic number densities from an absorption measurement requires high spectral resolution. Here, the narrow bandwidth of external cavity diode lasers is used to obtain the spectral behavior in the cesium ground state populations in the ablation plume.

Spectral line shapes have been investigated since the first observations of LIP and have been more and more thoroughly studied in view of the possibility of obtaining high spectral and temporal resolution simultaneously. Numerous examples of measurements that follow the LIP evolution of spectral line shapes have been commonly used and reported in the literature. Emission spectroscopic detection is the most common method of linewidth measurement. For
example, Német et al.\textsuperscript{103} studied the structure of spectral lines of Au, Ag and Cu lines at various delay times from several alloys. Hermann et al.\textsuperscript{104} made a detailed study of the temporal and spatial development of LIP spectra of Ti in a N$_2$ atmosphere. Although emission spectroscopy has the advantage of not requiring a second radiation source, several properties make other diagnostic methods advantageous in line shape determination. At early times, the continuum emission produces a strong background and the temperature and number density are so high that the lines are generally self absorbed and/or self reversed. These effects complicate the determination of the true linewidth and make it difficult to extract plasma parameters. Even at later delay times, resonance lines or lines with strong transition probabilities are likely to be affected by self-absorption. On the other hand, in absorption spectroscopy, line shapes can be extracted directly if the laser power is low enough so that the transition is not saturated.\textsuperscript{65} Furthermore, the determination of the ground state lineshape is not possible in emission spectroscopy. Saturation spectroscopy requires a different treatment than the simple absorption theory.\textsuperscript{105} Measurements of $^{87}$Rb/$^{86}$Rb have been made using a continuous wave Ti-sapphire laser for atomic absorption measurements with laser sampling using a 1064 nm Nd-YAG laser.\textsuperscript{106} Dominant line broadening mechanisms for Ca and Rb in low pressure LIP have been determined by Gornushkin et al.\textsuperscript{99}. Another similar approach to measure line shapes is fluorescence spectroscopy and diode laser excited atomic fluorescence was used by Smith et al.\textsuperscript{107} for isotopically selective measurements in uranium plasmas.

In absorption spectroscopy, the concentration of the species is based upon measuring the difference between two large signals obtained in the presence or in the absence of the analyte. Such measurement is accomplished by either tuning the source on and off resonance or by continuously tuning the source wavelength over the resonance. A common approach to improve
the dynamic range in absorption spectroscopy is to use wavelength or frequency modulation. A diode laser is driven to smoothly modulate the wavelength over the spectral line at a certain frequency in the kHz-MHz range. Rather stable plasma generated in furnaces or in ICP can benefit from modulation spectroscopy; however, with the steep temporal gradients occurring in LIP, modulation frequencies of the order of 100 MHz are required and are not easily reachable with modern diode lasers.

**Theory Considerations**

The absorbed intensity, $I_A$, of a probe beam of light propagating through a linearly absorbing medium may be described by the Beer-Lambert relationship, given by

$$I_A = I_0 - I_t = \int_{\text{line}} I_0(\nu)(1 - e^{-k(\nu)\ell})d\nu$$

(4-1)

where $I_0(\nu)$ and $I_t(\nu)$ are the spectral distributions of the incident and transmitted radiant intensities (W cm$^{-2}$), $k(\nu)$ (cm$^{-1}$) the absorption coefficient depending of the atomic spectral line at frequency $\nu$ and $\ell$ (cm) the absorption path length. Spectral lines are never strictly monochromatic and a spectral distribution exists near the central wavelength. The atomic profiles are a function of the number of absorbing particles present in the plasma and can give distinct information about electron number densities and broadening mechanisms. The Full Width Half Maximum (FWHM) is often used to define the line profile and is the wavelength interval of a spectral line between two points whose intensity is equal to half of the maximum intensity.

The overall experimental line shape is a convolution of the line profile in the plasma and the linewidth of the probe beam. In the case of high-resolution diode lasers, equivalent to the ones utilized in this work, the external-cavity provided such high resolution that the probe beam bandwidth was much narrower than the probed line profile. Therefore, $k(\nu)$ is constant over the
source profile, and equal to its maximum value, \( k_m \). Thus the radiant intensity absorbed is given by

\[ I_A = (1 - e^{-k_m \ell}) I_S \]  

(4-2)

where \( I_S \) the intensity of the probe light integrated over its emission line width. For low values of the product \( k_m \ell \), i.e., at low optical densities, equation 4-2 simplifies as follows

\[ I_A \approx k_m \ell I_S \]  

(4-3)

The fraction of radiation absorbed, \( \alpha \), defined as the ratio \((I_A/I_0)\) is thus seen to be directly proportional to the peak value of the absorption coefficient. One can also relate the absorbance to the fraction of radiation absorbed through the relation

\[ A = \log \left( \frac{I_A}{I_0} \right) = -\log(1 - \alpha) \]  

(4-4)

Finally, from the classical radiation theory,\(^{96}\) and in the limit of low intensity of the exciting radiation, the absorption coefficient \( k(\nu) \) (cm\(^{-1}\)) can be expressed as

\[ k(\nu) = \frac{h\nu \gamma}{c} \cdot B_{lu} \cdot g(\nu) \cdot N_l \]  

(4-5)

Where \( h \) (J s) is the Plank constant, \( \nu_0 \) (Hz) is the central frequency of the transition, \( c \) (cm s\(^{-1}\)) is the velocity of light in vacuum, \( B_{lu} \) (J\(^{-1}\) Hz\(^{-1}\) cm\(^3\)) is the Einstein coefficient of stimulated absorption and \( N_l \) (cm\(^{-3}\)) is the number density of the absorbers in the lower energy level. The spectral distribution function is normalized, i.e. \( \int g(\nu) d\nu = 1 \). Integrating equation 4-5 over frequency, we have

\[ \int k(\nu) d\nu = \frac{h\nu_0}{c} \cdot B_{lu} \cdot N_l \]  

(4-6)

Or, by using the Einstein relations between \( B_{lu} \) and \( A_{lu} \):
\[ \int k(\nu) d\nu = \frac{\lambda_0^2 A_{ul}}{8\pi} N_l \] (4-7)

where \( A_{ul} \) (Hz) represents the Einstein coefficient for spontaneous emission between the upper level (\( u \)) and the lower level (\( l \)).

The lineshape function \( g(\nu) \) reflects the various broadening mechanisms occurring in the plasma.

**A Review of Broadening Mechanisms**

In laser induced plasmas, an atomic spectral line may be broadened due to Doppler and collisional broadening mechanisms. Because of the low laser fluence used in the present work, laser induced saturation and power broadening, which could be caused by the probe laser, are not considered. Doppler broadening, due to the relative motion of an absorbing particle and the light source, is particularly significant at the temperature common in atmospheric pressure plasmas. For a system of particles with a Maxwellian velocity distribution, the relation between the Doppler broadening FWHM, \( \Delta\nu_D \), and the kinetic temperature, \( T(K) \), is given by

\[ \Delta\nu_D = 7.16 \times 10^{-7} \nu_0 \sqrt{\frac{T}{m}} \] (4-8)

where \( T \) (K) is the temperature and \( m \) is the mass of the absorber (g). The line shape function exhibits a Gaussian shape described by:

\[ g_D(\nu) = \frac{2}{\Delta\nu_D} \sqrt{\frac{\ln 2}{\pi}} e^{-\left(\frac{\nu - \nu_0}{\Delta\nu_D}\right)^2} \] (4-9)

where \( \nu_0 \) is the central frequency and \( \Delta\nu_D \) is the FWHM.

Collisional mechanisms include van der Waals, resonance and Stark broadening and result in Lorentzian profiles. Van der Waals broadening is due to interaction between two neutral species, cesium and all neutral species, including cesium, not optically coupled to levels involved
in the probed transition. This is a short range force proportional to \( r^{-6} \) (attraction) and to \( r^{-12} \) (repulsion) described usually by the Lennard-Jones potential. This collision broadening can be diabatic or adiabatic. However, diabatic collision broadening is often overshadowed by adiabatic broadening which relates to collisions when the perturber does not induce a transition between atomic levels but causes a phase change of the emitting wavetrain. In the impact approximation, the collisional broadening FWHM and shift due to van der Waals interaction are given by

\[
\Delta \nu_{v.d.\text{Waals width}} = 2.71 C_6^{2/5} v^{3/5} n 
\]

(4-10)

\[
\Delta \nu_{v.d.\text{Waals shift}} = 0.98 C_6^{2/5} v^{3/5} n 
\]

(4-11)

where \( v \) (cm/s) is the relative velocity, \( n \) (cm\(^{-3}\)) is the concentration of perturbing particles, and \( C_6 \) (cm\(^6\).s\(^{-1}\)) is the constant determined by the interaction potential. Resonance broadening, which is \( 1/r^3 \) dependent, is due to interactions with similar atoms and may have effective cross sections orders of magnitude larger than foreign gas kinetic cross sections. This mechanism may be significant when an excited atom (state \( p \)) interacts with an identical atom in a significantly populated state (state \( q \)) and when a strong electric dipole transition couples the two levels. The Lorentzian FWHM, due to resonance broadening is given by the relation

\[
\Delta \nu_{\text{res}} \approx \frac{3}{2} \left( \frac{g_p}{g_q} \right)^{1/2} \left( \frac{e^2 f}{2\pi \varepsilon_0 m_e v_0} \right) N 
\]

(4-12)

where \( g_p \) and \( g_q \) are the degeneracies of the two states involved, \( f \) is the oscillator strength of the resonance transition, \( e \) the electron charge (C), \( m_e \) is the mass of an electron (kg), \( \varepsilon_0 \) is the vacuum permittivity (J\(^{-1}\)C\(^2\)m\(^{-1}\)), \( v_0 \) is the central frequency of the transition and \( N \) (m\(^{-3}\)) is the population number density of state \( q \). Note that that equation 4-10 does not depend on the relative velocities of the colliding atoms and hence on the plasma temperature.
Stark Broadening, due to Coulombic interactions with charged particles, is a function of \( n_e \) and \( T_e \) and is often the most significant collisional broadening mechanism, especially at early delay times in the plasma evolution. Heavy elements, such as cesium, are generally influenced by the quadratic Stark effect which yields an approximately Lorentzian lineshape. In addition to broadening, an absorption band may be shifted in wavelength (Stark shift) due to interactions with electric fields. Pressure shift and Doppler shift may also be present but can be negligible compared to Stark shifts when \( n_e > 10^{15} \text{ cm}^{-3} \), a condition satisfied in atmospheric laser-induced plasmas. Theoretical Stark parameters, tabulated by Griem \(^{110}\), relate the broadening and shift of the spectral lines in plasmas to electron number density and temperature. For singly-ionized plasmas, the total theoretical FWHM due to quadratic Stark broadening, \( \Delta \lambda_{\text{Starkwidth}} \) (Å), and the total theoretical Stark shift, \( \Delta \lambda_{\text{Starkshift}} \) (Å), are given by the formulas \(^{110}\)

\[
\Delta \lambda_{\text{Starkwidth}} = 2\left(1 + 1.75 \times 10^{-4} n_e^{1/4} \alpha \times (1 - 0.068n_e^{1/6}T^{1/2})\right) \times 10^{-16} wn_e \tag{4-13}
\]

\[
\Delta \lambda_{\text{Starkshift}} = \left(\frac{d}{w} + 2.0 \times 10^{-4} n_e^{1/4} \alpha \times (1 - 0.068n_e^{1/6}T^{1/2})\right) \times 10^{-16} wn_e \tag{4-14}
\]

where \( n_e \) is the electron number density (cm\(^{-3}\)), \( T_e \) is the electron temperature (K), \( w \) is the electron impact parameter (Å), \( \alpha \) is the ion broadening parameter, and \( d/w \) is the ratio of shift to width (dimensionless). The true line function is then the convolution of the Lorentzian and Doppler contributions and is known as the Voigt profile.

**Experimental**

**Frequency Calibration by a Confocal Fabry-Perot Interferometer**

Interferometers serve a variety of purposes in laser spectroscopy, they aid in the measurement of absorption or emission line profiles as well as in the diagnosis of laser mode structure, linewidth, and performance.\(^{111}\) Perhaps more importantly, interferometers provide a high resolution frequency ruler to appropriately analyze atomic spectra. In this work, the probe
laser frequency is monitored by sending a fraction the beam into a confocal Fabry-Perot interferometer (FPI).

The varying transmission function of a FPI is caused by interference between the multiple reflections of the incident light between the two reflecting surfaces. Constructive interference occurs if the transmitted beams are in phase, and this corresponds to a high-transmission peak of the etalon. If the transmitted beams are out-of-phase, destructive interference occurs and this corresponds to a transmission minimum. The condition for constructive interference within a FPI is that the optical path is equal to an integral number of wavelengths of the incident light.\textsuperscript{112}

Specifically, a confocal FPI consists of two partially transmitting spherical mirrors precisely aligned to form a reflective cavity. The mirrors have equal radii of curvature ($r$) and are separated by a distance $d$ where $d = r$. In this work, spherical mirrors with a 50 cm radius of curvature (CVI Laser Corporation, Albuquerque, NM) 98% reflectivity from 850-920 nm, and $\lambda/10$ optical quality is used. The two mirrors were permanently fixed by a 50 cm quartz tube to provide a rigid FPI which, after initial mirror alignment, could be moved as the whole.

Given the mirror characteristics and neglecting spherical aberration, the free spectral range ($\delta \nu$), or frequency separation between successive interference maxima, can be determined from the following relation:

$$\delta \nu = \frac{c}{2d}$$ \hspace{1cm} (4-15)

where $c$ is the speed of light and $d$ is the distance between the mirrors. The theoretical free spectral range of the device was therefore 150 MHz.

The overall performance of an interferometer is quantified by its finesse ($F^*$). A higher finesse value is indicative of a higher resolution measurement. The total finesse of an interferometer is influenced by the optical and alignment imperfections of the device, stemming
from non-ideal reflectivity, surface quality and wedge angle. In a confocal device, the total finesse is mainly governed by the mirror reflectivity, $R$, which is given by the following relation, and to a lesser extent, by the surface quality, respectively.\textsuperscript{113}

$$F_{\text{refl}}^* = \frac{\pi \sqrt{R}}{1 - R} \quad (4-16)$$

The theoretical finesse of the device was approximately 9.9. The device was calibrated by comparison to the fine structure splitting of the cesium $6S_{1/2} \rightarrow 6P_{3/2}$ transition at 852.34nm from a sealed cell containing cesium at low pressure.

In a pure cesium vapor at room temperature, the hyperfine component of the $6S_{1/2}$ ($F = 3, 4$) $\rightarrow$ $6P_{3/2}$ ($F = 2, 3, 4, 5$) transition has a Doppler shape (cf. equation 4-9). Six hyperfine transitions exist between the cesium $6S_{1/2}$ and $6P_{3/2}$ states, labeled a, b, c, d, e and f in Figure 4-1\textsuperscript{114}. For each component $i$, $k(v)$, $\Delta\nu_D$ and $k_0$ are given by the following equations, respectively:

$$k^i(v) = k_0^i e^{\frac{v - v_0^i}{\Delta\nu_D^i}} \quad (4-17)$$

$$\Delta\nu_D^i = \frac{v_0^i}{c} \sqrt{\frac{2kT}{m}} \quad (4-18)$$

$$k_0^i = \frac{1}{\Delta\nu_D^i} \frac{\pi e^2}{mc} \cdot N_i f_i \quad (4-19)$$

The hyperfine shift ($v_0^i$) and oscillator strength ($f_i$) for each individual hyperfine component can be found in Figure 4-1. The total Doppler envelope of the weak component ($F = 3 \rightarrow F = 2, 3, 4$) and the strong component ($F = 4 \rightarrow F = 3, 4, 5$) was then calculated by adding each individual profile with their respective weights derived from the selection rules. The calculated Doppler envelopes are shown in Figure 4-2. The spacing between the centers of the weak and strong components is measured to be 8.77 GHz and it can be compared to the spacing from the experimental spectra with its fringes. The theoretical free spectral range of 150 MHz is
confirmed by the number of fringes, 58.6, corresponding to a spacing of 8.77 GHz. It should be noted that the non-linear dispersion of the fringes from the confocal FPI at the far edge of a single scan is minimal and is neglected in this study.

**Experimental Setup**

The experimental setup used to acquire resonant absorption spectrum in a LIP is shown in Figure 4-3. The radiation at 852 nm was provided by an external cavity diode laser with nominal (manufacturer specified) linewidths of 5 MHz, as reported in the previous chapter. An iris of 200 µm restricted the dimension of the probe beam to allow spatially resolved measurement. The radiation is sent through the plasma generated by a Nd-YAG laser and detected several feet away by a spectrometer composed of a classic Czerny-Turner monochromator (0.5 m, 1200 gr/mm grating blazed at 400 nm, Acton Research) and a PMT (R5108, Hamamatsu, Japan). The spectrometer is computer controlled and set at 852 nm. As opposed to an interference filter, a monochromator is chosen in experiments involving the PMT detection, to provide a higher spectral background rejection, mainly from the strong early continuum emission. The latter would saturate the non-gated PMT and the recovery time would prevent early delay time observations. The PMT output is amplified by a proprietary module from Jobin Yvon inc. with an approximately 10 ns rise time and recorded by a 500 MHz oscilloscope (TDS 520D series, Tektronix, Wilsonville, OR) connected to a computer by a GPIB controller (GPIB-USB-HS, National Instruments, Austin, TX). Single sequence oscilloscope traces were imported into Microcal Origin Pro 7.5 for data analysis. The recorded time-resolved transmission signals are converted to absorbance by the usual relation (4-4), where \( I_0 \) is determined by averaging 200 pretrigger data points.

The sample is mounted on a XYZ stage and placed in a vacuum chamber. For this work, 0.1% CsCl fused SiO\(_2\) pellets were solely used as they provided good reproducibility and fewer
particles ejection. It is important to note that both the vacuum chamber and the ablation laser are
mounted on a secondary XYZ stage so that the entire plasma can be translated without changing
the ablation parameters (i.e. focal length), while keeping the iris and detecting optics fixed.

To scan the diode laser, a waveform provided by a function generator (Model FG3C, Wavetek Meterman, Everett, WA) is applied to a piezoelectric element placed behind the tuning mirror in the laser cavity. While scanning, the 852.34 nm diode laser is operated in the current coupling mode. The current coupling function couples the piezo voltage and the injection current of the laser diode. The benefit of this coupling is to extend the mode-hop-free tuning range of the laser system. Typically, a 1V peak-to-peak triangular wave at a frequency of 10 Hz was used for frequency scanning. The triangle function provides a linear frequency scan. It was found that, if a lower frequency was driving the piezo element, the laser would suffer from a small frequency drift over several scans. Relative frequency calibration is achieved by directing a portion of the scanning beam into the previously described confocal FPI. Interference fringes are detected by a photodiode. Absolute frequency calibration is obtained by scanning over the absorption profile of the previously mentioned cesium low pressure sealed cell.

The 10 Hz scanning frequency of the diode laser is considered small compared to the reciprocal of the plasma lifetime in order to justify the assumption the diode laser frequency remained constant for the duration of the plasma absorption. During a scan of 100 ms, the radiation frequency of the laser is scanned over 20 GHz. If a plasma lifetime of 100 µs is considered, the laser frequency has varied only by 20 MHz, just four times the laser bandwidth. As a quasi-fixed frequency is generated within the occurrence of the observed phenomena, the TTL output of the function generator triggered the output of an adjustable pulse/delay generator (Model DG535, Stanford Research Systems, Inc) that finally triggered the pulsed laser. The
delay generator controlled the frequency at which the probe beam is absorbed in the plasma. An absorption profile is then obtained by discretely changing the pulse delay after every single laser shot. Every time the Nd-YAG laser is fired, oscilloscope traces from the low pressure cesium cell scan and the Q-switched output pulse are recorded to monitor the probe laser frequency, as shown on Figure 4-4.

Finally, a set of neutral density filters was used to insure that the interaction between the laser and the atoms was linear. To verify this assumption, absorption measurements were taken with and without neutral density filters and found to be the same, within the uncertainty of our measurement.

**Results and Discussion**

To determine the influence of the ambient gas environment on the cesium ground state population in the plasma plume, absorption measurements were performed at different pressures, i.e. 1 atm, 5 mbar, 0.5 mbar and 0.01 mbar. Different experimental regimes can be expected here. At the lowest pressure, due to the absence of ambient gas particles, the PMT measurements taken at different distances from the target surface are equivalent to Time-Of-Flight (TOF) measurements of the atoms released from the target and reaching the probe volume. As the pressure increases, the kinetic distribution of the species in the plume will be affected because of the interactions between the plume and the surrounding gas.

**TOF Measurements for a Pressure of 0.01mbar**

From the TOF measurements, relevant information regarding the time taken by a given atomic population to develop in a given energy state after the plasma creation can be obtained. Time-resolved absorbance spectra taken at two heights from the plasma surface, 1 mm and 2 mm are displayed in Figure 4-5. A height of 1mm means that the laser probe beam diameter is centered at 1.1 mm from the surface. The beam diameter is 200 µm. The graphs represents a
contour plot, where the x-axis is the time in µs, the y-axis the frequency in GHz and the color intensity represents the absorbance. The intensity scale is displayed next to the contour plot. The time evolution gives an insight on the velocity, hence the kinetic energy of the emitted particles. In addition, relevant parameters which help the interpretation of the mechanisms responsible for the plume absorption are obtained as well. From Figure 4-5, the absorption is maximal at approximately 0.4µs and decreases with time as the plasma temperature decreases.

TOF absorption data can be represented by a shifted Maxwell-Boltzmann distribution with a center of mass shifted as expected with the formation of a thermalized Knudsen layer according to the relation.\(^{115}\)

\[
A(t) = N\left(\frac{z}{t}\right)^3 \cdot \exp\left(-\frac{m(z - v_{cm}t)^2}{2RT_s t^2}\right)
\]

(4-20)

where \(N\) is an amplitude normalization factor that depends on the ground state number density, \(z\) is the height of the probe beam above the surface, \(v_{cm}\) is the center-of-mass velocity, \(T_s\) is the effective internal temperature of the directed beam of particles or sample temperature, \(m\) is the mass of the species, \(t\) the time. The Knudsen layer is the region within a few mean free paths of the target surface in which the particles vaporized, sputtered due to the laser collides due to high-number densities.\(^{115}\) In this region the Maxwellian formulation assumes that the speed distribution has equilibrated after propagating a short distance from the target surface, and that the signal is a direct measure of the concentration of the indicated species. Figure 4-6 gives a typical TOF profile recorded for Cs atoms in vacuum. The fit to the data is shown by the red line in the Figure 4-6 and is in relatively good agreement with the experimental TOF curve. The calculated parameters, center of mass velocity and temperature are calculated to be \(2.3 \times 10^5\) cm s\(^{-1}\) and 22000 K respectively. Those values are in agreement with similar measurements performed on other samples.\(^{76,\,116}\)
The spectral structure which can be deduced from Figure 4-5, coincides with the ground state absorption of cesium, the strong (F=4 → F = 3, 4,5) and weak (F = 3 → F = 2, 3, 4) components of the 6S_{1/2} state are clearly visible but not resolved (cf Figure 4-8 a)). The significance of the Doppler, Stark and van der Waals broadenings mechanisms can be estimated from the theoretical dependence of the cesium 852 nm line width and shift upon plasma temperature as shown in Figure 4-7. The temperature dependence of the Doppler line width is given by equation 4-8 and is assumed to be dominant; calculations of van der Waals broadening and shift (equations 4-10, 4-11) are carried out using a typical value of \( \sim 10^{-42} \text{ m}^6 \text{s}^{-1} \) for the parameter \( C_6 \) and calculations of the Stark width and shift were made using equations 4-13, 4-14. The parameters \( \varpi \), \( d/\varpi \), and \( \alpha \) were not available for the Cs 852 nm line but were assumed to be identical to the parameters for the Cs 894 nm line. As one can see from Figure 4-7, van der Waals collisional broadening only is important for large number densities of perturbing atoms (over \( 4 \times 10^{17} \text{ cm}^{-3} \)), and so van der Waals broadening is negligible except for pressures near atmosphere. The other possible broadening to be considered is resonance line broadening due to collisions of like species (Cs and Cs). Resonance broadening occurs when a high number density is present for a coupled state. There are several states coupled to the ground states and from Figure 4-7, one can see that the number densities of the excited states have to be of the order of \( 5 \times 10^{16} \text{ cm}^{-3} \) to contribute significantly. At a delay time of about 0.4 \( \mu \text{s} \), when most cesium is likely to be excited, this broadening might therefore be important.

Figure 4-8 a) shows the spectral behavior of the absorbance observed at a height of 1 mm above the surface and at a delay time of 0.4 \( \mu \text{s} \), together with that obtained from the reference cell. In the latter, the linewidth is purely broadened and has no spectral shift. A small shift, less than 0.5GHz, is observed but this value is limited by the precision of the measurement. As one
can see from Figure 4-7, for Stark broadening to be dominant over the Doppler broadening (n_e > 10^{15} \text{ cm}^{-3}), a larger spectral shift would have been observed. Van der Waals broadening is not dominant for the same reason. The noise in the data makes an accurate fit to a Voigt profile difficult due to the complexity of the line, cf. six hyperfine components. The frequency scanning range of the diode laser barely resolves the spectral profile and contribute also to the uncertainties of the fitting. Several combinations of Doppler linewidth and Lorentzian line width can gave satisfactory results in the range of the experiment uncertainty, approximately 10%. The relative standard deviation was obtained from the data discussed in the previous chapter. For that reason, both Lorentzian and Doppler shapes were fitted to obtain the limiting case values. As can be seen from the Figure 4-8 a), Doppler fits better the tail of the absorbance profile. Pure Lorentzian lines resulted in a FWHM of 6 GHz and pure Doppler lines in a FWHM of 2.5 GHz. Both fittings give similar values for the number density of ground state that can be extracted from the line peak absorbance. The expression used for the peak absorbance in our case can be derived from equation 4-3, 4-5 and 4-7, and is given by the relationship

\[ A = k_m \ell = \frac{A_u \lambda^2}{8\pi} \cdot \frac{N_i \cdot \ell}{\Delta \nu_{\text{eff}}} \]  

(4-21)

where \( \Delta \nu_{\text{eff}} \) (Hz) is the effective line width of the absorption profile and is defined as

\[ \Delta \nu_{\text{eff}} = \int \frac{k(\nu) d\nu}{k_m} \]  

(4-22)

The effective line width is determined as the width of a rectangular line profile which has the same height and area as the real line. The absorption pathlength, \( \ell \), was estimated from absorption images to be 1 mm. The temporal evolution of the number density is shown in Figure 4-8 b). Number densities of 10^{16} \text{ cm}^{-3} are calculated A Doppler FWHM corresponds to a kinetic
temperature of $13000 \text{ K} \pm 1500 \text{ K}$ (cf. equation 4-6), a value commonly reported in the literature for similar plasmas at early delay times.$^{99}$

Therefore, on the basis of the set of data for Cs, Doppler broadening is the main contributor to the cesium 852 nm line width. Although Stark broadening exists, cf. the small shift in the lineshape, it is indistinguishable from resonance broadening as all the population of all the states involved are not known and have not been measured here.

**TOF Measurements for Pressures of 0.5 mbar, 5 mbar, 1 atm**

As the pressure is increased, gas phase collisions dramatically change the evaluation dynamics of the ablation plume and a double peak structure in the temporal profiles of the cesium ground state species is observed. Absorbance profiles recorded at various locations in the plume, 0 mm, 1 mm and 2 mm in a direction perpendicular to the target surface are given in Figure 4-9 and Figure 4-10. The time evolution as well as the spectral absorption profile obtained at 0.5 mbar, 5mbar and 1atm is plotted in a contour plot. In Figure 4-10, the time-resolved absorbance at the peak of the strong hyperfine component (at 1 mm for 0.5 mbar) clearly reveals that the cesium ejected by the plume exhibits a double peak TOF distribution. The first peak in time appears at approximately 0.4 $\mu$s for every pressure. The velocity of the particles sputtered and vaporized from the first peak is sufficiently high that the ambient gas pressure has a shifted Maxwellian distribution. The center-of-mass velocity is calculated as $1.4 \times 10^5 \text{ cm s}^{-1}$ and the surface temperature as 20000 K. However, the broadening of the peak is smaller. The kinetic temperature was calculated as (done previously) and found to be $8000 \text{ K} \pm 1000 \text{ K}$. This lower value is indicative of the surrounding gases slowing down the TOF particles. It should be noted that the Doppler lineshape fits better than the Lorentzian, supporting the idea of Doppler broadening as the dominant broadening.
The “second” absorption occurs at a different time, depending on the pressure and the height of observation, as shown in Figure 4-9 and 4-10. The time scale displayed is adjusted and is thus different for each pressure in order to follow the full time evolution. The time spacing between the two peaks, decreases from 0.5 mbar and 5 mbar. This is in agreement with morphology observations from the previous chapter. As the pressure increases, the plume is characterized by a strong interpenetration of the plasma species and the background gas leading to a thermalization of the species with their surroundings. Recombination reactions result in the formation of atoms and consequently induced the absorption observed. At 0.5 mbar, due to the low collisional environment, thermalization occurs from approximately 2 µs to 10 µs. After 10 µs, the plasma has cooled and no absorption is observed. At 5 mbar, the surrounding gases force the absorbing species to be contained into a smaller volume. Recombination occurs sooner and the absorbance is greatly enhanced. At atmospheric pressure, the apparent delay in the recombination process at 0 mm seems to indicate the occurrence of strong vorticity effects. The plume front is lifted from the surface and only after a long delay time, for example 20 µs in this case, the species closed to the surface absorb. The contour plot at 2 mm for 1 atm is not shown because the absorption was not resolved and absorbances greater than 1.5 are obtained. In this spatial region of the plasma, optically thick condition exists and a spectroscopic analysis could not be made.

The spectral broadening at 0.5 mbar and 5 mbar is dominated by Doppler broadening after the first peak occurs. According to Figure 4-8, which compares the different widths, one can see that Stark Broadening is not dominant with respect to Doppler broadening because of the absence of the Stark shift. As one can see from Figure 4-8, at high electron number densities, on the order of $10^{16}$ cm$^{-3}$, the Stark shift of the Cs 852 nm line is approximately 2 GHz. Therefore,
the upper limit for the electron number density, for delay >5 µs, can be estimated to be no more than approximately $10^{15}$ cm$^{-3}$. The same reasoning can be applied to indicate the absence of van der Waals broadening. A remaining possibility is resonance line broadening; however, the number density of resonant excited states has to be greater than $10^{16}$ cm$^{-3}$ for resonance broadening to be important. If we assume that Local Thermodynamic Equilibrium (LTE) conditions exist at a time delay of 2 µs and later, the states are in thermal equilibrium following a Boltzmann distribution and high temperature (>$10000$ K) are required to possibly achieved such high number densities for even the first excited state. Figure 4-11 shows Doppler fitting for different heights, the calculated kinetic temperature and the calculated cesium ground state number density.

At 1 atm, the confinement of the plasma species in the front part of the plume and the shielding generated by the steep gradient of pressures enhance the absorption of the cesium ground state. Temperature and number densities calculated are much higher in the confinement region. Doppler broadening is likely the main broadening mechanisms but Stark, van der Waals and resonance can all contribute to a Lorentzian broadening. A published work at atmospheric pressures reported contributions of 0.85 and 0.25 for Doppler and Lorentzian fractions, respectively, at atmospheric pressure. The authors made use of curve of growth methodology associated with absorption measurements to close estimate the ratio of the two broadening mechanisms. Doppler line shapes are fitted to atmospheric data and displayed in Figure 4-12.

Conclusions
Laser atomic absorption with a narrow band scanning diode laser has been used to evaluate laser plasma diagnostics at different pressures. So it was shown that, in the case of a trace element (cesium in a fused silica matrix), Doppler broadening is the dominant broadening mechanism. The number density of cesium atoms in the ground state, as well as the kinetic temperature is
evaluated by measuring line profiles and peak absorptions at 852 nm. Overall, high resolution measurements of the hyperfine structure of cesium under different experimental conditions have been illustrated. It is felt that the combination of time-resolved morphology measurements with high resolution spectral profiles data, as demonstrated in this work, represents an attractive tool for the diagnostics of laser induced plasmas.
Figure 4-1. Partial energy level diagram of cesium. The hyperfine structure of the $6S_{1/2} \rightarrow 6P_{3/2}$ transition are detailed. The diagram shows frequency detuning from the line center of each hyperfine component involves in the transition as well as relevant wavelengths and oscillator strengths.\textsuperscript{114}

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Figure 4-2. Calibrated dispersion of the confocal FPI.

58.5 fringes = 8.77GHz
Figure 4-3. Schematic of the experimental setup for time-resolved high-resolution absorption of the cesium ground state line at 852nm.
Figure 4-4. Records of the absorption profile of the cesium reference cell and the Q-switched output trigger from the pulsed-laser. The Q-switched trigger signal allows scanning through the profile by adjusting the gate on the pulsed-delay generator.
Figure 4-5. Contour plot of time-resolved spectra of the cesium absorption at a pressure of 0.01 mbar. The diode laser beam probes a 200 µm in diameter region at a) 1 mm and b) 2 mm from the target surface.
Figure 4-6. Typical TOF profile recorded by absorption of Cs atoms in vacuum and the shifted Maxwellian fitting.

\[ T_s = 22000 \text{K} \]
\[ V_{cm} = 2.3 \times 10^5 \text{ cm/s} \]
Figure 4-7. Calculated contributions of the spectral line width, and shifts, in GHz, for the Cs 852nm line, as a function of plasma temperature.
Figure 4-8. Absorption spectra and time-resolved ground state number density. Comparison of the absorption spectrum of Cs at 0.4 µs for a pressure of 0.01 mbar and the absorption spectrum of the reference cell in a). The frequency between the two peaks corresponds to the hyperfine structure. Gaussian and Lorentzian line shapes are fitted to the spectra. Time-resolved number densities in b) of the cesium ground state for two heights of observation calculated from peak absorption values.
Figure 4-9. Contour plot of time-resolved spectra of the cesium absorption at a pressure of 0.5 mbar and 5 mbar. The diode laser beam probes a 200µm in diameter region at 0mm, 1mm and 2mm from the target surface.
Figure 4-10. Contour plot of time-resolved spectra of the cesium absorption at a pressure of 1 atm. The diode laser beam probes a 200µm in diameter region at 0 mm and 1 mm from the target surface.
Figure 4-11. Effect of the distance from the probe beam to the sample surface on absorption spectra at 0.5mbar and 5mbar. The Gaussian fitting is shown on red at 4 μs and 3 μs delay, respectively.
Figure 4-12. Effect of the distance from the probe beam to the sample surface on absorption spectra at 1 atm. The Gaussian fitting a 30 µs delay is shown on red.
CHAPTER 5
INTRODUCTION TO ATOMIC VAPOR DETECTION

There is a growing need towards the development of photon detectors with high spectral resolution. Many applications such as laser Doppler velocimetry, chemical imaging and long-range optical communications require or can be enhanced by superior spectrally-resolved detectors. Atomic vapor detection is characterized by spectral discrimination in the range of MHz- GHz, or approximately $10^{-4}$ nm, in the near-infrared region. Several devices can detect photons with high spectral resolution, however, these detectors often lack other critical figures of merit such as high throughput, sensitivity, spatial resolution and image quality. High spectral resolution is achieved by exploiting the absorption features of atomic lines in their gas phase. Atomic vapor cells have been extensively used as ultra-narrow Notch filters, but their application as photon detectors is still limited. The potential applications of resonance detectors was described by Matveev et al. The primary absorption process occurring in the atomic vapor can be monitored by either detecting the fluorescence or the ionization resulting from a selected state, usually excited with a laser. Imaging can be accomplished by spatially expanding the excitation laser into two dimensions.

Single-point photon detectors are resonance ionization detectors (RID) and resonance fluorescence detectors (RFD). Several versions of these detectors have been described based on the atomic vapors, mercury and cesium for both single-point photon and imaging detection. However, the different types of detection are based on the same operating principle. Figure 5-1 depicts the general operation of a resonance fluorescence detector and a resonance ionization detector. Fluorescence photons or electrical charges are created and only detected when the interrogated object emits or scatter radiation of an energy matching exactly that of the narrow absorption linewidth of the atomic transition chosen and is summarized in Figure 5-2. In
a fluorescence detecting scheme, the signal photons at the resonance absorption wavelength, $\lambda_1$, which are absorbed, excites ground state atoms to the first excited energy level. Photons outside the narrow absorption band pass through the cell unaffected. Excited atoms can further be excited by a pump laser tuned to a second transition at the wavelength, $\lambda_2$. For imaging detection, $\lambda_2$ is expanded into a sheet of light and directed into the side of the cell behind the input window. Excited atoms decay to the fluorescent level and emit at the wavelength, $\lambda_F$. This fluorescence can be detected using a CCD camera for imaging or PMT or photodiode for single point. Due to the difference in wavelength between $\lambda_1$ and $\lambda_F$, a standard optical filter or a dichroic mirror for back-fluorescence, can be used to spectrally separate $\lambda_F$ from the unabsorbed photons. The ionization detector works in similar fashion; however, the photoionization of excited atoms requires a multistage excitation from two lasers, $\lambda_2$, $\lambda_3$. Electrons created in the plane of these two lasers are accelerated toward a microchannel plate (MCP) by the high voltage applied between the input window and MCP. Electrons striking the MCP are amplified and transfer from the electric field to phosphorous screen from which a image is captured by a CCD.

Because all atomic vapor photon detectors have a fixed frequency of detection, a tunable source of light is required to investigate the phenomenon. Photon detection occurs by tuning in wavelength the incident light such that that upon interaction with an object or phenomenon, the scatter light will be shifted into resonance with the transition of the atomic vapor. Any phenomenon that generates wavelength shifts upon interaction with incident radiation, Mie scattering, Raman scattering, Doppler velocimetry, can benefit from these detectors.

Different transition schemes in the case of multiphoton excitation have been tested. A mercury based RID was first demonstrated by Matveev et al. $^{122}$ A three-step ionization scheme was used with the first transition, $\lambda_1$ at 253.7 nm. Electrons created from photoionization were
directly directed toward a luminescent screen by a voltage applied between the screen and input window. The mercury RID was further improved by the addition of a microchannel plate. A compact sealed-cell Hg RID was also reported where an image composed of 1000 photons was detected by image summation. The spectral resolution obtained was on the order of 25 GHz due to the combination of Doppler-broadened profiles of seven mercury isotopes.

The use of cesium as the atomic vapor has several advantages. Both cesium and mercury possess high vapor pressures at room temperature but cesium has only one stable isotope so its absorption profile is not complicated by isotope spectral shifts. The ground state transition for cesium has a large oscillator strength (f=0.72) and occurs in the infrared which is beneficial for several ways. Wavelengths in the near infrared are accessible by external cavity diode laser which are spectrally narrow, tunable, inexpensive and small; as opposed to UV radiations used to reach Hg resonance transition. Large excimer- or Nd-YAG-pumped, pulsed dye laser systems are used to produce a tunable UV source. In addition, near-infrared can effectively penetrate biological tissues with minimum photodegradation, enabling potential applications in biological and medical fields. The near absence of native fluorescence in this region is another advantage in detecting Raman scattering.

Temirov et al. described a cesium based RID in a six-way cross vacuum chamber. The detector consisted of a metal coated vapor input window, a commercially available alkali metal vapor dispenser and a MCP-phosphorous screen. The excitation/ionization scheme \(6^2S_{1/2} \rightarrow 6^2P_{3/2} \rightarrow 8^2D_{3/2} \rightarrow \text{ionization continuum}\) was employing radiation at 852.34 nm, 917.47 nm and 1064 nm. A portion of the Nd-YAG laser was used to pump a Raman wavelength shifter and the resulting radiation was directed into a second harmonic generation crystal. The second harmonic at 599 nm pumped a color center crystal which could simultaneously produce 852.34
and 917.47 nm. The spectral resolution of the detector was limited by the Doppler-broadened linewidth of the signal transition and determined as 540 MHz. A major limitation of the cesium RID is the reactivity of cesium. Despite considerable effort in constructing the device to overcome the reactivity, the detector had only a limited lifetime of about a week before the electrodes and windows required cleaning. The coating left by cesium on the surface caused a decrease the threshold voltage before an arc was created between the atom chamber and the electrodes, thus limiting its operation.

A cesium based RFD has been described by Korevaar et al. The RFD was based on a two-step excitation scheme \((6^2S_{1/2} \rightarrow 6^2P_{3/2} \rightarrow 8^2S_{1/2})\) followed by wavelength-shifted fluorescence at 455.35 nm \((7^2P_{3/2} \rightarrow 6^2S_{1/2})\). A spectral resolution of 600 MHz was reported at the working temperature of 100°C. The Cesium RFD uses commercially available absorption sealed-cells as the atomic vapor reservoirs. RFDs provide the advantage of being compact, inexpensive and do not require any maintenance. The dimension of a sealed Cs RFD cell varies from few millimeters to tens of centimeters depending on the application desired. The most recent RFD was reported by Pappas et al., who used the same first resonance excitation as the detector radiation but further excited the \(6^2P_{3/2}\) state by pumping to the \(6^2D_{5/2}\) state by laser excitation at 917.47 nm, \(\lambda_2\). The excited atoms radiatively decay to the \(7P_{3/2}\) and subsequently generate fluorescence photons at 455.65 nm. A limitation of the cesium RFD is the relatively low sensitivity when compared to high-gain devices with poor spectral resolution such as acousto-optic tunable filters or liquid crystal tunable filters. Correll et al. devoted a significant effort in increasing the quantum efficiency of the process by collisional excitation energy transfer. Pixley et al. used the latter cesium resonance fluorescence detector for moving-object detection where they measured Doppler-shifted radiation (cf. Figure 5-3 a)). Velocity differences of 15 m/s could be resolved
and working detection range of up to 1500 m/s was available given the tuning characteristics of the first excitation laser. Pappas et al.\textsuperscript{132} used the same RFD to detect Mie scattering from silica particles by deconvolution of Mie scatter from the instrumental response (cf. Figure 5-3 b)). The Mie scattering linewidth (140 MHz) correlated well to the literature value of 100 MHz in air.

Another type of scattering, namely Raman scattering, has been investigated, mainly because of the versatility and quantitative ability of the Raman technique. However, while Mie scattering benefits from the high spectral resolution of the detector and the high number of signal photons available, Raman scattering does not. In fact, the Raman linewidth is much larger than the absorption linewidth and the scattering cross section is very small. The number of Raman photons detected is limited and thus, an excellent limit of detection in terms of number of photons is required.

The goal of this work is to further develop cesium-based vapor detectors by simplifying the detection process for practical use and to focus towards the detection of Raman photons.
Figure 5-1. Schematic of a resonance fluorescence detector and resonance ionization detector. In a), when the radiation $\lambda_1$ is absorbed, the atoms excited are further excited to a fluorescing state by a radiation $\lambda_2$. The fluorescence photons can be detected at the back of the cell after going through a standard optical filter. In b), when the radiation $\lambda_1$ is absorbed, $\lambda_2$ and $\lambda_3$ ionized the excited atom. The ions or electrons are accelerated and amplified in the MCP by a voltage between the input window and MCP. The electrons hit the phosphorous screen and are converted to photons. The latter are detected by a CCD.
Figure 5-2. The principle of operation of an atomic vapor photon detector, the atomic vapor absorbs at fixed frequency. A tunable source is required to interrogate the frequency shift from the moving object or species that scatter light inelastically.
Figure 5-3. Applications of a cesium RFD. Fluorescence excitation profiles of the reference beam and scatter representing different disk velocities in a), adapted from 131. The measurement of Mie scattering from a particulate solution in b): spectral response of the RFD; scattering signal detected from a suspension of particles; deconvoluted Mie spectrum. 132
CHAPTER 6
ATOMIC VAPOR DETECTORS: TOWARD THE DETECTION OF RAMAN SCATTERING PHOTONS

Introduction

Raman spectroscopy is a powerful tool capable of providing information about the structure, properties and concentration of molecules. Its major disadvantage is that of having a very weak signal due to the small cross section of the interaction process. In fact, the Raman cross section is approximately 12-14 orders of magnitude lower than the competitive effect, fluorescence. The fundamentals and applications of Raman spectroscopy has been reported extensively in the literature and can be found in several reviews and books. Most of the scientific studies in the field of Raman research were and still are, performed as single point non–imaging methods. Compact lasers, notch filters, and CCD cameras revolutionized the field in the late 1990s. From a single point scanning method, Raman spectroscopy has developed into a two dimensional chemical and biological imaging technique. Several instruments are available for a variety of applications. Imaging Raman spectroscopy is advantageous when high fidelity images at a limited number of wavelengths (in the simplest case one wavelength) provide sufficient chemical and spatial information. Reducing the number of spectral channel decreases the time necessary for 2-D experiments without losing spatial distributions and is of high interest for fixed wavelength detectors as atomic vapor detectors.

Although several versions of Raman imaging devices are commercially available, there is still considerable room for improvement in the field, which can be addressed with the further development of atomic vapor detectors (AVD). It is important to note that the spectrally selective atomic vapor detectors do not require filtering of stray radiation that might occur at the excitation wavelength, since only Raman scattered radiation corresponding to the narrow absorption profile of atoms will be detected.
The detection of Raman photons by means of laser-enhanced ionization was experimentally demonstrated for the first time by Smith at al.\textsuperscript{139} Magnesium was chosen as the atomic vapor due to its efficient atomization in an air-acetylene flame, and Raman scatter from carbon tetrachloride molecules were detected. A tunable dye laser was scanned around the resonance transition of Mg at 285.213 nm. Further excitation with a second laser and subsequent collisional ionization in the flame resulted in the creation of ion/electron pairs. Raman spectra of dimethyl sulfoxide, carbon tetrachloride, and chloroform were also successfully recorded with a Mg flame resonance ionization detector.\textsuperscript{140}

The use of atomic vapors as spectrally selective filters has also been demonstrated to reject Rayleigh scattering.\textsuperscript{141} Rb and Hg vapors formed in a furnace were used to filter Raleigh scattered radiations from carbon tetrachloride samples. Continuous wave Ti-Sapphire laser at the 794.76 nm resonance transition of Rb and XeCl excimer pumped dye laser at the Hg resonance line at 253.64 nm interrogated the Raman active samples.

One point of concern in the detection of Raman signals with low pressure atomic vapor detector, such as a resonance ionization detector (RID), is that the typical spectral bandwidth of Raman scatter is much larger than the Doppler-limited absorption profile of atomic vapor at room temperature. Typically, the Raman band half width, $\Delta \lambda_R$, is in the range of 30-50 cm$^{-1}$ while the atomic linewidth, $\Delta \lambda_I$, is about 400 MHz ($\sim$0.01 cm$^{-1}$). Because of this spectral discrepancy, the absorption efficiency will decrease proportionally with the ratio $\Delta \lambda_I / \Delta \lambda_R$ and so will the background-limited signal-to-noise ratio, which is proportional to the square root of $(\Delta \lambda_I / \Delta \lambda_R)$.

To better illustrate this point, the theoretical background that includes a comparison of Raman signal levels expected from an atomic vapor detector (AVD) (fluorescence or ionization)
as compared to a conventional Raman spectrometer is useful to our approach. The Raman signal, 
\( S_R \) (in counts) for the spectrometer is given by the following relation:

\[
S_R = \left( E_p \left( \frac{d\sigma}{d\Omega} \right)_a N_a \right) \left[ A_D \Omega \right] T(\eta_D) t \tag{6-1}
\]

Here, \( E_p \) is the laser photon irradiance (photons \( s^{-1} \) \( cm^{-2} \)), \( \left( \frac{d\sigma}{d\Omega} \right)_a \) is the Raman differential cross section of the analyte molecules (\( cm^2 \) \( sr^{-1} \)), \( N_a \) is the number of scattering molecules per unit area (\( cm^{-2} \)), \( A_D \) is the useful area of the detector (\( cm^2 \)), \( \Omega \) is the collection solid angle (\( sr \)), \( T \) is the transmission factor of the optical system, \( \eta_D \) is the detector efficiency (counts/photons) and \( t \) is the integration (measurement) time (s). The first product (within braces in the above equation) corresponds to the excitation efficiency and the second represents the optical conductance or luminosity of the spectrometer.

In this approach, the Raman signal will be given by:

\[
(S_R)_{AVD} = \left( E_p \left( \frac{d\sigma}{d\Omega} \right)_a N_a \right) \left[ A_D \Omega \right]_{AVD} T(\eta_D)_{AVD} t \tag{6-2}
\]

The terms and symbols are the same as in equation 6-1 and the suffix AVD has been added. By comparing the two equations, and assuming equal values of the optical transmission, as well as equal integration times, we can see that

\[
\frac{(S_R)_{AVD}}{S_R} = \frac{(A_D \Omega)_{AVD}}{A_D \Omega} \frac{(\eta_D)_{AVD}}{\eta_D} \tag{6-3}
\]

The first ratio on the right hand side of equation 6-3 represents the ratio of the optical conductances, \( \xi_{en} \). This ratio can be much larger than unity, indicating that the optical conductance of AVD can be much larger (typically \( 10^4 \) times higher) than of a conventional Raman spectrometer, for the same spectral resolution. This clear advantage of AVD has been
reported by Matveev et al.\textsuperscript{121}. Most type of spectrometers can be designed to provide a high resolving power, $R \ (R=10^6-10^8)$. However, for most spectrometers, increasing the resolving power inherently comes at the expense of the luminosity. Table 6-1 shows some values for the luminosity, resolving power and their product.

It is clear that, in theory, atomic vapor detectors largely surpass the performance of the other detection systems. Atomic vapor detectors are quantum devices and atoms inside the cell are isotropically sensitive to resonant photons. The luminosity is then constant and independent of $R$.

From equation 6-3, one can see that if $\eta_D$ for a conventional spectrometer detector system is assumed unity, $(\eta_D)_{AVD}$ must equal to $(\xi_{en})^{-1}$ for AVD to detect the same number of Raman photons as the traditional Raman spectrometer.

The overall detection efficiency of an AVD system is given by the product of several efficiency factors, namely the absorption efficiency or fraction absorbed, $\eta_{abs}$, the fluorescence efficiency, $\eta_F$ (or ionization efficiency, $\eta_{ion}$ for RID), and the collection efficiency, $\eta_c$ (of photons for RFD or electrons for RID). In an AVD working under vacuum, the absorption efficiency is bound to be low due to the large difference in the spectral profiles of Raman emission and atomic absorption. It is clear that in this case both the ionization (or fluorescence) efficiency and collection efficiency need to be closed to unity; otherwise the gain due to high luminosity is completely counter-balanced. The improvement of these efficiency factors dictates our approach in this work. First, a new cesium fluorescence detection scheme with the presence of an ethane buffer gases improves the fluorescence efficiency. Second, the absorption efficiency is improved by broadening the absorption bandwidth with helium as a buffer gas.

It should be reported that some efforts were first dedicated to improve the cesium resonance ionization detector previously developed in our laboratory.\textsuperscript{125} Although theoretically
superior to RFD, the practical and successful implementation of cesium ionization imaging remains a task facing several engineering challenges. High ion collection efficiency in a Cs-RID detector requires a low working pressure to avoid recombination of the formed ions while they are accelerated to the multichannel plate. The consequently low (~$10^{-4}$) absorption efficiency require the ionization efficiency to be close to unity. The ionization efficiency depends upon the excitation-ionization scheme chosen and the laser power available. A 100% efficiency can be reached if the second excitation step (917 nm) and the photoionization step (wavelengths >744 nm) are both saturated. If a commercially available Alexandrite/LiF:F$_2^+$ laser matched the requirement and improved the efficiency, ultimately, the high reactivity of cesium with all the different components of the detector prevented the RID from working in proper conditions. A major change in the materials used or design had to be performed and therefore our focus was shifted to RFD using sealed cells.

**Improvement of the Fluorescence Efficiency, $\eta_F$**

Fluorescence efficiency of $10^{-3}$ have been reported for RFD described by Pappas et al.\textsuperscript{124} based on the two-step detection scheme, $(6^2S_{1/2} \rightarrow 6^2P_{3/2} \rightarrow 6^2D_{5/2})$: absorption at 852 nm, excitation at 917 nm followed by fluorescence detection at 455 nm. The fluorescence efficiency was limited by the radiative coupling from the $6^2D_{5/2}$ to $7P_{3/2}$ states required from fluorescing at 455 nm and all the other coupled state that decreases the quantum efficiency. A novel cesium fluorescent detecting scheme is developed in this work that does not require a second step excitation. Photons matching the ground state transition at 852 nm ($6^2S_{1/2} \rightarrow 6^2P_{3/2}$) are collisionally coupled to the $6^2P_{1/2}$ state that is resonant with the ground state, and fluorescence occurs at 894 nm. The transition $6p^2P_{1/2} - 6p^2P_{3/2}$ is forbidden by the selection rules, hence the coupling has to be induced by collisions. For this coupling to be efficient, a very fast mixing rate is required to overcome the large difference in energy between the two states, 554.1 cm$^{-1}$ and
ethane was chosen for this purpose. Recently, Beach et al.\textsuperscript{142} developed an end-pumped cesium vapor laser based on the same approach with high average power that potentially competes with diode-pumped solid-states lasers in applications that required cw operation.

Single step detection significantly decreases the complexity of the atomic vapor detector, while several strong lasers to saturate the resonant transitions are no longer required. Many applications that required small and compact instrument can greatly benefit from the development of this simple fluorescence detector.

**Investigation of Ethane-induced Collisional Energy Mixing in Cesium**

Several studies have focused on collisional energy mixing in laser excited alkali vapors using noble gas perturbers, involving Cs-He and Cs-Ar.\textsuperscript{114} In a low pressure cesium cell that does not contain ethane, the relaxation rate from the $6^2P_{3/2}$ level to the $6^2P_{1/2}$ is slow compared with the $3.3 \times 10^{7}$ s$^{-1}$ natural decay rate out of the $6^2P_{3/2}$ level (30.5 ns lifetime), which decays radiatively back to the ground state $6^2S_{1/2}$ level by means of an electric dipole allowed transition. The requirement for this rapid fine-structure mixing is the reason for the presence of ethane in the cell. Krause et al.\textsuperscript{143} measured the cross-sectional values for the Cs $6^2P_{3/2} \leftrightarrow 6^2P_{1/2}$ population transfer by collision with various hydrocarbons to be in the order of $10^{-15}$ cm$^2$. The participation of the molecular rotational degrees of freedom of ethane in the energy transfer accounts for the very large magnitudes of the mixing cross sections. The cross section was found 4 to 6 orders of magnitude larger than similar cross sections for collisions with noble gases\textsuperscript{143}. In this work, the cross-section value of the cesium-ethane mixing from $6^2P_{3/2} \leftrightarrow 6^2P_{1/2}$ is determined by measuring the fluorescence intensity of both the radiation at 894.6nm and 852.6nm when excited by a laser at 894.6 nm and at 852.6 nm.
Fluorescence Intensity

Fluorescence photons are directly related to the fraction of radiation absorbed. The fluorescence intensity from a specific state, $I_F$, excited by a monochromatic source of intensity, $I_0$, is described according to the relation below a line source assuming excitation and no pre- or post-filter effects

$$I_F = Y I_0 (1 - e^{-k_m \ell})$$  \hspace{1cm} (6-4)

where $k_m$ is the peak absorption coefficient (cm$^{-1}$), $\ell$ (cm) is the absorption pathlength, $I_0$ the intensity of the input radiation (W.cm$^{-2}$) and $Y$ is the fluorescence power yield, given by the ratio between the spontaneous emission from state $j$ to state $i$, $A_{ji}$, and the sum of all the deactivation channels from level $j$, including collisions, $R_{jq}$.

$$Y = \frac{A_{ji}}{\sum_q A_{jq} + R_{jq}}$$  \hspace{1cm} (6-5)

If the product $k_m \ell$ is much smaller than 1, which is the case for low number densities, the absorption system is optically thin and the previous expression can be simplified as followed

$$I_F = Y I_0 k_m \ell.$$  \hspace{1cm} (6-6)

In the above equation, $k_m$ is given by the expression

$$k_m = \frac{A_{nl} \lambda_0^2}{8\pi \Delta \nu_{eff}} \frac{n_l}{\Delta \nu_{eff}}$$  \hspace{1cm} (6-7)

where $n_l$ is the number density of perturbers (cm$^{-3}$), $\Delta \nu_{eff}$ (Hz) is the effective width of the absorption.

The measured fluorescence signal finally depends on the solid angle of detection, $\Omega_c$, the collection and efficiency of the detector (counts/photon), $\varepsilon$, and the probed volume (cm$^3$), $V$, and is given by the expression
\[ S_F = \varepsilon \frac{\Omega c}{4\pi} V I_F \]  

(6-8)

**Rate equation Approach**

The steady-state and temporal behavior of laser interaction with an atomic system are often described by either the rate equation formalism or the density matrix formalism.\(^{144}\) The density matrix formalism properly provides the more complete description of laser excited atomic systems. It properly treats coherence effects resulting from the finite bandwidth of a laser source interacting with a broader absorption profile. It can also describe certain effects caused by narrowband light at high intensities, such as dynamic Stark effects (broadening and splitting of levels) and two-photon excitation.\(^{145}\) In general, those effects are significant whenever high intensity, narrowband light excites atoms in a weakly collisional media. For collisional media, with external cavity diode laser, the rate equation approach gives a reasonable description.

The principle of detailed balance states that the number of atoms per second leaving the considered quantum state, \(a\), through any particular process must equal the number of atoms per second entering that state, i.e. \(\frac{dN_a}{dt} = 0\), where \(N_a\) is the population of the state \(a\). This balance holds for collisional processes and is individually applicable to each pair of levels. For each state an equation can be written to describe the change on the corresponding population due to all the radiative and non radiative processes which are present. For a considered state \(a\),

\[
\frac{dN_a}{dt} = \sum_i P_{ia} N_i - D_{ai} N_a
\]

(6-9)

where \(P_{ia}\) is the radiative and non radiative rate of population of the state \(a\) from state \(i\), \(D_{ai}\) is the radiative and non radiative probability of depopulation from the state \(a\) to state \(i\). For the non radiative or collisionally induced transition, the corresponding transition probability is given by
the rate $R_{mm'}$, where $m$ and $m'$ are the initial and final state from the collisions between A and B. This rate is directly proportional to the number density of perturber atoms, $N_k$. In analogy with gas kinetics, the rate $R_{mm'}$, is also proportional to the mean relative velocity of the colliding atoms A and B:

$$R_{mm'} = \sigma_{mm'} \bar{V}_{rel} N_k$$  \hspace{1cm} (6-10)

Under typical experimental conditions i.e., in cesium absorption at room temperature, the distribution of atomic velocities is Maxwellian and the temperature-dependent mean relative velocity of the Maxwellian distribution is given by the relation

$$\bar{V}_{rel} = \sqrt{\frac{8k_B T}{\pi \mu_{A-B}}}$$  \hspace{1cm} (6-11)

where $k_B$ is the Boltzmann constant, $T$ is the temperature of the system and $\mu_{A-B}$ is the reduced mass of A-B quasimolecule formed by a collision between the two atoms. In equation 6-7, the proportionality constant $\sigma_{mm'}$ with the dimension of area is the cross section of the process. In general, cross sections for electron excitation energy transfer depend on the relative velocity and are therefore functions of the system temperature.

In this work, as the cross sections from cesium-ethane is orders of magnitude higher than from cesium-helium, the latter are neglected. Another assumption made is to neglect the quenching from helium and ethane. Figure 6-1 summarizes the rates involved in the level scheme when the cesium sealed is pumped by the $6^2S_{1/2} \rightarrow 6^2P_{3/2}$ transition at 852.6 nm. $B_g$ is the stimulated emission coefficient and $\rho$ the energy density of the laser.

The steady state rate equation for the level 1 ($6p^2P_{1/2}$) when level 2 is pumped by the radiation at 852 nm is

$$\frac{dN_1}{dt} = R_{21} N_2 - A_{10} N_1 - R_{12} N_1 = 0$$  \hspace{1cm} (6-12)
Thus the number density ratio is equal to
\[
\frac{N_2}{N_1} \bigg|_{852} = \frac{(A_{10} + R_{12})}{R_{21}}
\] (6-13)

If we now look at the fluorescence ratio from equation 6-8, we obtain
\[
\frac{S_{F2}}{S_{F1}} = \frac{\varepsilon_2 \Omega_c V I_{F2}}{\varepsilon_1 \Omega_c V I_{F1}}
\] (6-14)

If the two input radiations at 852.4 nm and 894.6 nm are co-linearly propagating in the cell, the fluorescence will be detected by the same collection optics. The efficiency of the detection system is assumed constant over the range of the two transitions. Furthermore, the power of the two lasers are monitored and adjusted to the same value with a set of neutral density filters. Consequently, the previous equation can be simplified, and by substituting \( I_F \) from equations 6-6 and 6-7, the detected fluorescence ratio is obtained
\[
\frac{S_{F2}}{S_{F1}} = \frac{A_{20}}{A_{10} + R_{21}} \frac{A_{10} + R_{12}}{A_{20}} \frac{\lambda_{20}}{\lambda_{10}} \frac{A_{20} N_2}{A_{10} N_1} \frac{\Delta V_{eff1}}{\Delta V_{eff2}}
\] (6-15)

Since the effective width of the two transitions is derived from the same Doppler and Lorentzian broadening parameters, they can be considered identical. Finally, the following equations enable a direct calculation of the cesium-ethane rate, \( R_{21} \) and \( R_{12} \), and therefore their cross sections assessing the efficiency of the coupling, by solving the ratios of intensity fluorescence
\[
\frac{S_{F2}}{S_{F1}} \bigg|_{852} = \frac{(R_{12} + A_{10})}{R_{21}} \frac{A_{20} \lambda_{20}}{A_{10} \lambda_{10}} \left( \frac{1 + \frac{R_{12}}{A_{10}}}{1 + \frac{R_{21}}{A_{20}}} \right)
\] (6-16)
\[
\frac{S_{F2}}{S_{F1}} \bigg|_{894} = \frac{R_{12}}{(R_{21} + A_{20})} \frac{A_{20} \lambda_{20}}{A_{10} \lambda_{10}} \left( \frac{1 + \frac{R_{12}}{A_{10}}}{1 + \frac{R_{21}}{A_{20}}} \right)
\] (6-17)
The experimental tabulated values for $A_{20}$ and $A_{10}$ are respectively $2.86 \times 10^7$ s$^{-1}$ and $3.28 \times 10^7$ s$^{-1}$.

**Experimental Setup**

The cross sections for cesium $6^2P_{3/2} \leftrightarrow 6^2P_{1/2}$ mixing in cesium vapor were investigated in a series of fluorescent experiments in a sealed cell as shown in Figure 6-2.

The absorption sealed cell in this experiment, measuring 25 mm in diameter and 40 mm in length was commercially procured (Optos Instruments, Inc, Rockville, MD) with uncoated optical windows on each end and filled at room temperature with 100 Torr of ethane and 350 Torr of He, in addition to a small quantity of cesium metal prior to be sealed off. The temperature of the cell varied from room temperature to 150°C by a current-controlled heating tape wrapped around the cell and is further monitored by a thermocouple. Higher temperature were not attempted as the inside pressure of the cell would exceed atmospheric pressures and could compromise the integrity of the cell.

The cesium atoms were excited from ground state to, alternatively, $6P_{1/2}$ and $6P_{3/2}$ state by two diode lasers. A flipping mirror enables alternating from the 894.59 nm laser diode -operated in Littrow external cavity (model TEC-100, Sacher Lasertechnik, LLC, Marburg, Germany) to a 852.34 nm diode laser operated in a Littman-Metcalf external cavity (Model TEC-500, Sacher Lasertechnik, LLC, Marburg, Germany). Both laser beams were collimated and superimposed. An iris was used to restrict the radiation diameter to a common value of 2mm, providing a homogeneous radial intensity distribution over the entire cell. The stability of the laser radiation was monitored by PMT detector (R636, Hamamatsu, Japan). The PMT output was amplified (Model 427, Keithley Instruments, Cleveland, OH) and recorded by an oscilloscope (TDS3000 Series, Tektronix, Willsonville, OR).

The fluorescence was collected from the input window at an angle by a fiber optic and sent to an Ocean Optics spectrometer (crossed Czerny-turner monochromator with a CCD detector.
calibrated for 770 nm to 1030 nm). The spectra were recorded with different integration times and the results shown were normalized in Counts/second for comparison of different spectra.

The resonance fluorescence signal was corrected for the scattering of the incident light which mainly occurred from input window of the cell. An optimum collection angle was experimentally found where the fluorescence/ scatter ratio is maximal, due to the different distributions of the fluorescence and the scattering. The remaining scattering was corrected by subtracting the recorded spectrum with the laser detuned from the cesium transition.

Results

Figure 6-3 shows the fluorescence spectra measured from 852 nm and 894 nm excitation radiations. The fluorescence intensities are derived from the two spectra and the measurement is repeated several times with different collection angles and different wavelengths. The total pressure of the cell is 450 Torr, the main broadening mechanism is collisional broadening, more precisely van der Waals broadening (cf. chapter 4). When the laser is scanned over the transition, the fluorescence intensities vary but the ratio remains constant. The effect of the laser power is shown in Figure 6-4 and confirms that the atomic system was not saturated. The ratio for several temperatures is displayed in Table 6-2 and the calculated values of $R_{12}$, $R_{21}$ and the cross section $\sigma_{21}$ (cm$^2$) are summarized in Table 6-3. The calculated cross section are in the same order of magnitude as the values obtained by Krause et al. confirming the fast mixing induced by ethane molecules. For the cesium-ethane cell, the fluorescence efficiency is calculated to be 0.09 (cf. equation 6-5) and is 2 orders of magnitude higher compared to previous RFD.

Improvement of the Absorption Efficiency

As stressed before, the absorption efficiency of the Raman photons is bound to be low for RFD operating at low pressure. When the cesium absorption profile is pressure broadened, a significant improvement is expected. Figure 6-5 shows the Raman signal and the expected signal
absorbed for a low pressure cell dominated by Doppler broadening at 25 °C. Raman lineshape can be described by a Lorentzian profile and a 30 GHz bandwidth (1 cm\(^{-1}\)) was chosen for the sake of the argument. The fraction absorbed was calculated to be approximately 10\(^{-4}\). The pressure of the different buffer gases was selected to give an absorption linewidth similar to that of a Raman signal. In addition of 100 Torr of ethane, 350 Torr of He was added to further broaden the absorption linewidth. The broadening processes already described in chapter 4 are used here to calculate the theoretical linewidth. It should be noted that, in our experimental conditions, the main source of collision broadening results from the interaction of cesium atoms with helium, ethane and other cesium atoms, i.e.

\[ \Delta v_L = \Delta v_{Cs-Cs} + \Delta v_{Cs-ethane} + \Delta v_{Cs-helium} \]  

(6-18)

The individual contributions to the total Lorentzian width, \( \Delta v_L \), were calculated using the values for the reduced broadening constant \( \gamma = \Delta v_L / n \) where \( n \) is the number density of perturbers. These values are listed below:

\[ \gamma_{Cs-Cs} = 6.7 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \]
\[ \gamma_{Cs-He} = 3.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \]
\[ \gamma_{Cs-ethane} = 50 \text{ MHz/Torr} \]

The values used for the perturber number densities were 2.4 \times 10^{10} \text{ cm}^{-3} for the cesium vapor cesium and 3.13 \times 10^{19} \text{ cm}^{-3} for 350 Torr of helium.

**Experimental**

The experimental setup is shown in Figure 6-6 and the measurements were carried out at room temperature, 25°C. The radiation at 852 nm was provided by an external cavity diode laser with manufacturer-specified linewidths of 5 MHz as described in the previous chapter. A waveform provided by a function generator (MODEL FG3C, Wavetek Meterman) was applied
to a piezoelectric element placed behind the tuning grating in the laser cavity. A portion of the scanned laser beam was directed to a custom-built confocal Fabry Perot interferometer to monitor the wavelength emitted by the laser. The radiant intensity transmitted through the cell is directed into a 852 nm interference filter (Optometrics, LLC) and detected by a Photomultiplier tube (R636, Hamamatsu) sensitive in the near-infrared.

The potential use of this RFD as an image detector is measured by expanding the beam to the dimension of the cell, then by passing through a transmission target (USAF 1951 3-Bar Resolving Power Test Target). The resulting image was then passed through a dielectric mirror positioned at 45° that transmit at 852 nm and reflect a fraction of the 894 nm radiation which is sent into the RFD cell previously described. The fluorescence photons passing through an interference filter at 894 nm (Optometrics, LLC) were imaged onto the photocathode surface of a single-stage, proximity focused image intensifier (MODELV807OU-64-N132, Hamamatsu Corporation, Japan). Photons emitted from the phosphor-coated back surface were imaged onto a cooled, digital CCD camera (Model Penguin 150CL, Pixera Corporation, Los Gatos, CA) with integration times from 0.1 ms to 60 s.

Results

Because of collisional broadening, the RFD absorption bandwidth is estimated to be approximately 15 GHz and verified experimentally; however, as shown in Figure 6-7 a), the mode-hop free range is limited to 25 GHz and a proper correction for the baseline is difficult as the profile is not resolved. Difficulty with baseline correction is enhanced by the distortion of the baseline from etalon effects every time the laser radiation passes through a surface. With a bandwidth of 15 GHz, the fraction absorbed for a Raman signal of 1cm⁻¹ was estimated to be 0.4. This is three orders of magnitude higher than from a low pressure RFD. The fraction absorbed is improved at the cost of the imaging performance as shown in Figure 6-7 b). The high collisional
environment blurs the fluorescence images. It should be noted that measurements at higher
temperature increases the fraction absorbed as the number density of cesium in the vapor phase
increases.

**Overall Performance of an AVD for Raman Detection**

The different efficiencies of the cesium/ethane RFD have been estimated and the number
of photons to be detected can be calculated from equation 6-2:

\[
(S_R)_{AVD} = \left( E_p \left( \frac{d\sigma}{d\Omega} \right)_a N_a \right) \left( A_D \Omega \right)_{AVD} T_{AVD} (\eta_D)_{AVD} t
\]  

(6-2)

We assume a laser photo irradiance, \( P \), of \( 10^{16} \) photons s\(^{-1}\) cm\(^{-2}\) (10 mW cw laser), a differential
cross section, \( \left( \frac{d\sigma}{d\Omega} \right)_a \), of \( 10^{-29} \) cm\(^2\) sr\(^{-1}\), a number of scattering molecules per unit area, \( N_a \), of
\( 10^{19} \) molecule cm\(^{-2}\), a luminosity, \( A_D \Omega \), of 0.12 and an optical system transmission factor, \( T \), of
unity. The detector efficiency for our particular RFD is the product of the measured fluorescence
efficiency, 0.09, the fraction absorbed, 0.4 and the secondary collection/detection efficiency
estimated to be 0.08. By combining these values a photon rate of \(~100\) photon/s needs to be
detected by the secondary detector. Several detectors, mainly photodiodes have the potential to
measure such low signal in the near infrared at 894 nm but were not available in our laboratory.
Moreover, the estimated photon rate represents the higher “ideal” limit of detection and an order
of magnitude higher should be required to hopefully detect Raman photons. The optical
transmission factor was assumed equal to unity and the spectral bandwidth of Raman scatter is
more, typically for biological systems, in the order of hundreds of GHz, further reducing the
absorption efficiency.
Conclusions and Remarks

A simple, compact cesium resonant fluorescent detector has been developed. The detection scheme is based on the absorption of the ground state atoms at 852 nm (6^2S_{1/2}→6^2P_{3/2}) and fluorescence decay from the 6^2P_{1/2} state. A buffer mixture of ethane and helium improve the detector efficiency by several fold compared to previously reported RFD. Ethane collisionally coupled the 6^2P_{3/2}-6^2P_{1/2} states, very fast mixing rate were measured (mixing across sections in the order of 10^{-15}cm^2, and fluorescence efficiency was improved by two orders of magnitude. Helium collisionally broadens the absorption bandwidth and fraction absorbed was improved by three orders of magnitude. However, the primary goal, detecting Raman scattering photons have not been successfully reached. Raman scattering is characterized by a low cross section and large emission spectral linewidth compared to AVD.
Figure 6-1. Schematic of the different rates involved in the $^6{}^2S_{1/2} \rightarrow ^6{}^2P_{3/2}$ detection process. The cesium atomic vapor is pumped by a 852 nm laser radiation. In this figure, the radiative absorption and emission rates due to stimulated processes are indicated as $B_{ji}\rho$ where $B_{ji}$ is the Einstein coefficient for stimulated absorption (emission) and $\rho$ the energy density of the laser.
Figure 6-2. Experimental setup to measure the fluorescence response of an atomic vapor cell. The cell contains 350 Torr of helium and 100 Torr of ethane from a 852 nm and 894 nm diode laser radiation.
Figure 6-3. Fluorescence spectra of a cesium-ethane absorption cell. The cell is excited by a) a 852 nm laser radiation and b) a 894 nm laser radiation. The spectra were corrected for scattering.

Figure 6-4. Effect of the laser power on the fluorescence intensity (Log-Log scale)
Figure 6-5. Calculated Raman linewidth and corresponding signal absorbed. Spectra are shown for a) a low pressure cesium cell and b) a cesium cell containing 100 Torr of ethane and 350 Torr of helium at 50°C.
Figure 6-6. Experimental setup for measuring the spectral absorption lineshape of the RFD and evaluate its imaging performance.
Figure 6-7. Spectral profile and image of the Cs/ethane RFD at room temperature. Absorption spectrum, a) and image of the 852 nm laser radiation through the transmission mask, b). No signal was measured when the laser was detuned from the transition.
### Table 6-1. Values for several detectors of the luminosity, Resolving power and their product.

<table>
<thead>
<tr>
<th>Spectrometer</th>
<th>LR</th>
<th>R_{max}</th>
<th>L (cm^2 sr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interference filter</td>
<td>0.1</td>
<td>10^4</td>
<td>10^{-5}</td>
</tr>
<tr>
<td>Grating monochromator</td>
<td>1</td>
<td>5 \times 10^5</td>
<td>2 \times 10^{-6}</td>
</tr>
<tr>
<td>Fabry-Perot interferometer</td>
<td>100</td>
<td>10^6</td>
<td>10^{-4}</td>
</tr>
<tr>
<td>Atomic vapor detector</td>
<td>8 \times 10^{10}</td>
<td>8 \times 10^8</td>
<td>100</td>
</tr>
</tbody>
</table>

### Table 6-2. Fluorescence ratios at different temperature

<table>
<thead>
<tr>
<th></th>
<th>25 °C</th>
<th>45 °C</th>
<th>55 °C</th>
<th>65 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>852 pump</td>
<td>S_2/S_1</td>
<td>0.288</td>
<td>0.278</td>
<td>0.298</td>
</tr>
<tr>
<td></td>
<td>std dev</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>894 pump</td>
<td>S_2/S_1</td>
<td>0.227</td>
<td>0.253</td>
<td>0.279</td>
</tr>
<tr>
<td></td>
<td>std dev</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
</tr>
</tbody>
</table>

### Table 6-3. Calculated mixing rates and cross sections of Cs 6^2P_{3/2} ↔ 6^2P_{1/2} induced by 100mTorr of ethane

<table>
<thead>
<tr>
<th>T, °C</th>
<th>R_{12} (s^{-1}) ± 0.5 \times 10^8</th>
<th>R_{21} (s^{-1}) ± 0.8 \times 10^8</th>
<th>\sigma_{21} (cm^2) ± 0.3 \times 10^{-15}</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>3.2 \times 10^8</td>
<td>8.0 \times 10^8</td>
<td>3.3 \times 10^{-15}</td>
</tr>
<tr>
<td>45</td>
<td>4.5 \times 10^8</td>
<td>9.8 \times 10^8</td>
<td>4.2 \times 10^{-15}</td>
</tr>
<tr>
<td>55</td>
<td>6.4 \times 10^8</td>
<td>1.2 \times 10^9</td>
<td>5.2 \times 10^{-15}</td>
</tr>
<tr>
<td>65</td>
<td>6.7 \times 10^8</td>
<td>1.4 \times 10^9</td>
<td>5.9 \times 10^{-15}</td>
</tr>
</tbody>
</table>
Future work in the field of atomic vapor photon detection and imaging can be done in the improving the sensitivity and expanding the range of applications.

Atomic vapors have been used as absorption or notch-like filters; for example, to discriminate against Rayleigh scattering in Raman spectroscopy. These filters can provide less expensive alternatives to commercially available holographic notch filters. In this work, an atomic vapor detector based on cesium resonance fluorescence has successfully improved the detection efficiency but has not yet reached the sensitivity needed to detect Raman scattered photons. A solution to increase the number of Raman photons is to use Raman enhancing techniques. In the past decades, Surface Enhanced Raman Spectroscopy (SERS) has shown promise to overcome the traditionally low sensitivity of normal Raman spectroscopy.

Studies have been made to understand the signal enhancement observed when a molecule is attached to various metals such as silver, gold and copper. The signal enhancement has been increased by 14 orders of magnitude making single molecule detection possible. This signal enhancement would translate into a Raman cross section of approximately $10^{-16}$ cm$^2$/molecule. There are two operative mechanisms responsible for the SERS phenomenon, namely electromagnetic field enhancement and chemical enhancement. The former contributes to the enhanced Raman signal when scattering takes place in the enhanced local optical fields of the metal and the latter is due to metal-molecule interaction. An example of SERS was explored in our laboratory, as a tool to study biological agents. Dipicolinic acid is an important biomarker used for detection of bacterial spores and the feasibility of SERS in a continuous flow mode has been evaluated. With the signal enhancement of SERS, AVD can be exploited as Raman photon detectors.
Bakker et al. have proposed another application for the use of atomic vapor absorption filters in the field of plasma diagnostics, namely in the detection of Thomson scattering.\textsuperscript{152} There is significance to the determination of number density ($n_e$) and temperature ($T_e$) of free electrons in a plasma as a function of time and space. These measurements can provide information concerning the details of energy transfer and departures from equilibrium. Electron number density also play a role in excitation and ionization mechanisms as well as plasma viscosity, electrical and thermal conductivity.\textsuperscript{153}

A common method of monitoring electron number density in analytical plasmas uses Stark broadening of the absorption or emission lines of the plasma gas (cf. Review of Broadening in chapter 4, equation 4-12). The method, as discussed in chapter 4, is complicated by the need to distinguish Doppler broadening and the instrumental response function. Electron number density and temperature have also been determined by absolute line intensity measurements of two or more of the plasma gas emission lines. In this method, the determination of $n_e$ and $T_e$ are dependent so errors in one results in error in the other. Emission in this technique can only be laterally resolved and plasma symmetry must be assumed which is not always the case.

Langmuir probes have been used in plasma diagnostics. In general, these probes are relatively inexpensive and provide adequate spatial resolution. In practice, however, they can only be applied to low temperature, low pressure plasmas and the probe is likely to disturb the plasma during measurements. Sheath formation around the probe, probe heating, and probe erosion have also hindered this technique.\textsuperscript{153}

J.J Thomson presented the theory for the scattering of electromagnetic radiation by electrons in 1907.\textsuperscript{154} The phenomenon, however, was not studied in the laboratory until decades later with the advent of intense laser sources capable of producing appreciable scattering from
high electron number density plasmas. Thomson scattering was then used in the study of high
temperature plasmas used in nuclear fusion research and later applied to processing plasmas.
Hiefte et al. \textsuperscript{155} have since applied the techniques to study analytically relevant plasmas including
microwave plasmas and the inductively coupled plasma or ICP.

As J.J. Thomson theorized, when an incident laser beam interacts with a charged particle in
a plasma, the oscillating field of the radiation induces the charge to oscillate in resonance with
the field. The oscillating charge radiates light, a phenomenon also known as Thomson scattering.
The wavelength of this scattered radiation that reaches a detector is double Doppler-shifted as the
radiation is moving rapidly with respect to both the source and the detector. In general, the width
of the Thomson scattering spectral profile is related to the velocity and therefore $T_e$ while the
area of the spectrum is related to the $n_e$.\textsuperscript{153}

Detecting Thomson scattering requires excellent stray light rejection and spectral
discrimination; the small cross section of this event ($6.7 \times 10^{-25} \text{cm}^2$) results in a weak signal as
compared to the intensity of the source required to produce the scatter. The optical system used
to collect the scattered light is usually a double or triple monochromator. However, the use of
these low throughput systems is not useful in the detection of weak Thomson scattering signals
from low density plasmas. An alternative method has been described for the detection of weak
Thomson signals. Bakker et al. have demonstrated the use of a sodium vapor absorption cell or
“atomic notch filter” placed between the plasma and the detector.\textsuperscript{152} Scattered light was collected
and directed through the vapor which absorbed the stray light and Rayleigh scattering at the
incident wavelength. This approach allowed broadened Thomson scatter to be transmitted and
detected by conventional means. The main current constraints of this application are the high
laser power necessary (hundreds of mJ) and plasma with relative high electron number density.
Laser induced plasmas ($n_e > 10^{16} \text{cm}^{-3}$) can be investigated with Nd-YAG laser with 200mJ/pulse as excitation source. The developments of atomic vapor-based devices will certainly aid the application of Thomson scattering detection.
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BIOGRAPHICAL SKETCH

Benoît Lauly was born in Paris, France on November 16, 1979. He spent his early years in Reims, Champagne-Ardennes region, France. Benoît graduated from the Ecole National Supérieur de Chimie et Physique de Bordeaux (ENSCPB) in 2003. While attending at the ENSCPB, Benoît did 6 months internship in the analytical department of Agfa-Gevaert N.V, Antwerpen, Belgium. He enrolled at the University of Florida in August 2003 in the chemistry graduate program and received his PhD in August 2008 under the supervision of Dr James Winefordner. He accepted a postdoctoral position at Duke’s biomedical engineering department under Dr Tuan Vo Dinh’s supervision.