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Inner-shell excitation of atoms for the development of short wavelength laser sources

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Rice University, 1989
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INNER-SHELL EXCITATION OF ATOMS FOR THE DEVELOPMENT OF SHORT WAVELENGTH LASER SOURCES

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

MASTER OF SCIENCE

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ABSTRACT

INNER-SHELL EXCITATION OF ATOMS FOR THE DEVELOPMENT OF SHORT WAVELENGTH LASER SOURCES

by

Timothy W. Petersen

This work focuses on the feasibility of producing new short wavelength laser sources using inner-shell photoionization or shake-up excitation induced by laser-produced plasma pumping. Laser-produced plasmas effectively convert high energy laser pulses into incoherent light in the XUV and are suitable pumping sources for high energy transitions. An experimental apparatus was constructed appropriate for preliminary studies in both barium and helium. For barium, dye laser excitation of an appropriate target state was explored as an initial step towards efficient pumping of core-excited states of the barium ion. In helium, studies explored methods to reduce the resonant trapping of the He(II) ion which limits the ability to produce an inversion on the n=4-->2 transition and the n=3-->2 transition.
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# TABLE OF CONTENTS

Chapter 1: Introduction  
Laser-Produced Plasmas  

Chapter 2: Experimental Apparatus  
Introduction  
Spectra-Physics DCR-3 Nd:YAG Laser and PDL-2 Dye Laser  
Barium Heated Cell  
Helium Cell  
Vacuum Pumps  
Detection Equipment  
Vapor Pressure Measurements  

Chapter 3: Barium Experiments  
Introduction  
Theory  
Laser-Designated Photoionization  
Barium Photoionization  
Dye Laser Considerations  
Experimental Approach  
Experimental Results  
Discussion  
Future Experiments
LIST OF FIGURES

1.1 Spectral and temporal characteristics of a laser-produced plasma 5
1.2 Laser-designated photoionization laser 8
1.3 Energy levels of He(II) 10
2.1 Experimental apparatus 12
2.2 Temporal output of DCR-3 Nd:YAG laser 14
2.3 PDL-2 dye laser 16
2.4 Dye laser spectral characteristics 17
2.5 Focus size measurements 19
2.6 Barium vapor pressure curve 21
2.7 Scintillator fluorescence and photocathode quantum efficiency 25
2.8 Timing and wiring diagram for detection equipment 26
2.9 Equivalent width of an absorption curve 29
2.10 Vapor pressure measurements for rubidium 32
3.1 Excitation functions for barium 39
3.2 Energy levels for 71.2 nm emission 40
3.3 Electron photoionization cross sections for barium 47
3.4 Laser-designated photoionization in barium 50
3.5 Spectral characteristics of excited barium 59
3.6 Spectral characteristics of barium, 50-143 nm 60
3.7 Spectral characteristics of barium, 100-200 nm 61
3.8 Spectral characteristics of barium, 200-300 nm 62
3.9 Spectral characteristics of barium, 300-400 nm
3.10 Dye laser scan of 72.5 nm and 64.7 nm
3.11 Dye laser scan of 71.2 nm and 65.3 nm
3.12 Dye laser scan of 68.5 nm and 74.3 nm
4.1 He(II) energy levels
4.2 Resonant trapping in helium
4.3 Photoionization and shake-up
4.4 Trapping coefficient as a function He(II) density
4.5 Fluorescent intensity of 121.5 nm, 164 nm, and 468.5 nm
4.6 Peak intensity versus energy, 121.5 nm
4.7 Peak intensity versus pressure, 121.5 nm
4.8 Peak intensity versus pressure, 164 nm
4.9 Peak intensity versus pressure, 468.5 nm
4.10 Plasma temporal characteristics
4.11 VUV resonator
4.12 VUV resonator dimensions for solid angle
4.13 R versus energy, 121.5 nm
4.14 R versus pressure, 121.5 nm
4.15 R versus pressure, 164 nm
4.16 R versus pressure, 468.5 nm
4.17 Depletion of 468.5 nm transition at 0.5 Torr He
4.18 Gain length product versus R
<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Barium XUV transitions</td>
<td>37</td>
</tr>
<tr>
<td>3.2</td>
<td>L-S terms for $5p^56s5d$</td>
<td>46</td>
</tr>
<tr>
<td>3.3</td>
<td>Barium photoionization</td>
<td>49</td>
</tr>
<tr>
<td>3.4</td>
<td>Barium resonant ionic enhancements</td>
<td>56</td>
</tr>
<tr>
<td>3.5</td>
<td>Barium lines and identifications, 50-400 nm</td>
<td>64</td>
</tr>
<tr>
<td>3.6</td>
<td>Dirac-Fock mixing coefficients</td>
<td>71</td>
</tr>
<tr>
<td>4.1</td>
<td>Helium levels, n=1-4</td>
<td>79</td>
</tr>
<tr>
<td>4.2</td>
<td>Photoionization calculations for helium</td>
<td>85</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

Since lasers were first introduced in the 1960's there has been considerable interest in developing new laser sources to cover the electromagnetic spectrum. Nonlinear harmonic generation, as well as excimer systems, have produced lasers operating near 200 nm. It is desirable to develop systems which can operate in the region below 200 nm known as the vacuum ultraviolet, or VUV. An experimental consideration for lasers operating in the VUV is the broadband absorption of electromagnetic radiation below 200 nm by oxygen. This requires all VUV/XUV lasers to operate in either a vacuum environment or in a noble gas atmosphere whose broadband absorptive features lie at considerably shorter wavelengths. Due to the absence of transmitting materials, there are also considerable problems designing resonator systems for VUV/XUV lasers. Lasers must either operate above the cutoff for transparent materials, or as high gain, single pass lasers. It is the goal of this research to investigate possible laser systems operating in the VUV and XUV (extreme ultraviolet λ<100 nm) regions.

A wide variety of applications for lasers having wavelengths less than 200 nm exist. Imaging a very small object requires a source whose wavelength is of the same order as the object's dimensions. A decrease in the wavelength would result in a subsequent increase in the resolution, allowing imaging of small structures such as compact integrated circuit designs. A short
wavelength source would also be able to etch a substrate in patterns whose width would be limited to the same order as the wavelength, allowing further miniaturization of integrated circuit designs.

Despite the potential for these short wavelength sources, there are a number of problems which make the development of short wavelength lasers inherently difficult. Lasers generally use the energy from transitions in molecules or atoms. The criteria establishing which of these should be used depends on how energetic a transition is required. For infrared lasers, 0.1 eV - 1 eV is needed to generate light in the 0.8 μm to 10 μm region. For this wavelength region, rotational and vibrational transitions in molecules as well as some electronic transitions are suitable. For wavelengths in the visible, VUV, and XUV, 5 to 30 eV are needed, and thus electronic transitions are used to generate these higher energies. Very little is known, however, about many of the high energy transitions in atoms, especially transitions involving a core electron that has been promoted above the first ionization potential of the atom. Before designing a laser system in the VUV/XUV, one needs to consider the spectroscopy of these excited levels to learn more about their lifetimes, oscillator strengths, and relative branching ratios. The work presented here is directed towards the spectroscopy of atomic or ionic levels which appear promising for lasers in the VUV/XUV.

Perhaps the most important concern for the development of short wavelength coherent sources is a pumping source to produce these highly excited states. Empirically, it is known that the pump power required for a transition scales as the third or fourth power of
the transition frequency [1].

\[ P_{\text{pump}} \propto v^{(3-4)} \]

Producing highly energetic transitions requires a high power pump source. At Rice University, we have explored two possible pump sources for the generation of short wavelength sources.

The first of these is an electron beam machine which uses 1 MeV electrons to ionize and collisionally excite different atomic and gaseous media. Using this pump source, cells have been designed which are capable of maintaining temperatures up to 700 °C and alkali metal vapor pressures up to 10 Torr. High energy electrons are coupled into a cell containing atomic vapors through a thin (2 mil) Ti foil. During the course of this work, using these cells and mixtures of noble gases and alkali metal vapors, the ionic alkali excimer \((\text{Xe-Cs})^+\) has been observed at 172 nm [2,3,4].

Another excitation technique studied extensively at Rice University has been the use of laser-produced plasmas. Many commercially available laser systems use high energy flashlamps to pump the lasing media. To apply this methodology to short wavelength lasers, a suitable source of broadband radiation in the 1 to 100 nm regime is needed. A plasma produced by a high intensity laser beam on a solid target is an excellent candidate for approximating an XUV flashlamp [5].

**LASER-PRODUCED PLASMAS**

When an intense laser source is focused onto a target, electrons can gain enough energy through a multiphoton process to overcome
the work function of the material and are removed from the surface of the material. The increase in the number of electrons attenuates the incoming radiation through inverse bremsstrahlung until expansion of the plasma once again allows radiation to reach the surface and strip more electrons. The generation, heating, and expansion of the plasma takes place on a time scale short enough to allow the plasma to equilibrate itself with respect to the incoming radiation for incident laser pulses greater than 1 ns in duration [6].

The electrons in the plasma begin to lose their energy through collisions and radiative processes. The two most important of processes are the spontaneous emission of photons by the electrons in the field of ions (bremsstrahlung) and the emission of a photon when an electron recombines with an ion (recombination). The spectral characteristics of the plasma depend on the temperature of the electrons, which is in turn dependent on the intensity of the incident laser beam and the target material. The emission spectra from bremsstrahlung and recombination overlaps to form a continuum as shown in figure [1.1]. For experimental calculations it is possible to approximate these emissions as the emission from a blackbody having a temperature of 10-100 eV [7]. The emission from a plasma of a high Z material such as tantalum has a characteristic temperature $kT = 10-30$ eV [8] for an incident intensity of $2 \times 10^{11}$ W/cm$^2$.

Because of their ability to efficiently convert radiation into the XUV, laser-produced plasmas are an excellent approximation of the flashlamps used to pump other laser sources in the visible region.
Figure [1.1]. Spectral and temporal characteristics of a 10 ns, 1 J Nd:YAG laser-produced plasma on a tantalum target. Spectral scan shows a broad continuum in the XUV. The spectral scan is not corrected for the variation in grating reflectivity which accounts for the decline in signal below 50 nm.
The coherent radiation from the laser can be converted with a reasonably high efficiency (10-20%) [9] into incoherent radiation in the XUV region. A favorable characteristic of a laser-produced plasma is that the photoionization of a core electron has a high cross section for photons in the 10-50 eV range. For this reason, laser-produced plasmas are particularly attractive for studying core-excited states, where the excitation of a inner-shell electron is of primary importance.

Using a laser-produced plasma, three different systems have been studied during the course of this work. The first of these is the ionic alkali halide excimers, and excimers, (Xe-Rb)$^+$, (Xe-Cs)$^+$ and (Xe-F) which have been observed for the first time in a laser-produced plasma [10]. Secondly, the rare earth alkali metal barium, which has ionic transitions in the XUV, has been studied. Finally, the He(II) ion has been investigated to study the feasibility of producing a laser on the ionic transitions at 164.0 nm and 121.5 nm. This thesis focuses on the studies of photoionized barium and helium.

In the barium system, there is a strong emission in the Ba(II) ion which may be from a quasi-metastable state, namely, a state where an inner-shell electron has been excited above the first ionization threshold but has a high radiative rate due to angular momentum conservation which does not favor autoionization [11]. The upper level of the barium transition may be a core-excited state involving the ionization of a core electron and the excitation of an outer shell electron. In an effort to enhance the population of the
excited state, selective excitation of the ground state barium atoms prior to photoionization by a laser-produced plasma was studied. Because a laser-produced plasma is efficient at removing a 5p electron from the barium atom, it would be desirable to place the ground state barium atoms in a configuration isoelectronic to the upper level with the exception of a 5p electron. The excitation scheme used a dye laser to resonantly excite the ground state barium by tuning to an intercombination line having a high oscillator strength. In the lower manifold of the barium atom, the \((5p^66s6p)^3P_1\) level is coupled to the ground state allowing an intercombination transition at 7911 Å from the \(^1S_0\) ground state to the \(^3P_1\) level despite the change in spin \((S=0 \longrightarrow S=1)\). The \(^3P_1\) level populated by the dye laser should lase to the desired lower level which is isoelectronic to one of the proposed upper levels of the transition with the exception of an extra 5p electron. This designated lower level in Ba(I) is the \(5p^66s5d\ \ ^3D\) state and decays very slowly to the ground state of the atom because the transition involves a change \(ΔL=2\), and is therefore a quadrupole transition. The process in which the barium is excited by a dye laser beam and then photoionized by the laser-produced plasma, has been termed laser-designated photoionization and is depicted in figure [1.2]. Based on preliminary results obtained using dye laser preparation of the lower level and the information available at present, a tentative excitation mechanism and identifications for the previously unidentified barium emissions in the XUV have been assigned. Further
Figure [1.2]. Laser-designated photoionization laser. The ground state atoms are selectively excited by a dye laser to populate the designated level before being photoionized by a laser-produced plasma into the upper level.
application of this technique should prove useful establishing the upper and lower levels of the barium transition and may help in understanding the production mechanism to the upper levels of the core-excited Ba(II) transitions.

The ionic transitions in He(II), shown in figure [1.3], were also investigated to learn more about how the lifetimes are affected by resonance trapping. When helium is photoionized, the remaining electron may leave the ground state and occupy an excited state corresponding to a different principal quantum number, in a process known as shake-up. The natural lifetimes of the n=3 and n=4 states of the He(II) ion are much longer than the n=2 state. Inversion should be possible between these states if efficient pumping to the upper states can be achieved. The inherent problem in this system, however, is an apparent increase in the lifetime of the n=2 state through resonant reabsorption of the photons emitted in the n=2 ---> n=1 transition, known as resonance trapping. Initial experiments with a laser resonator are described.
Figure [1.3]. Energy level diagram for the He(II) ion showing the transition wavelengths and energies for the n=1 to n=4 states.
Chapter 2: Experimental Apparatus

INTRODUCTION

To investigate the systems of interest, spectroscopic studies of the VUV and XUV transitions of the atoms were undertaken. The basic experiment for all of the studies was to contain a vapor in an evacuated cell with pressures ranging from 0.1 to 30 Torr. For the helium studies, it was not necessary to heat the cell, as helium is a gas at room temperature. Barium, on the other hand, is a solid at room temperature and must be heated. For a vapor pressure of 0.5 Torr, the barium cell had to heated to approximately 1100 °C. To contain the barium vapor and to keep it from entering the spectrometer, helium was also introduced into the cell at a pressure approximately matching the barium pressure. The cell was operated as a heatpipe, maintaining a well defined boundary between the buffer gas and the barium [12]. Once a stable vapor pressure was established, a pulsed Nd:YAG laser was introduced into the cell and focused onto a tantalum target. The soft x-rays from the laser-produced plasma created on the target pumped the vapor in the cell. Spectral and time-integrated information were collected by a VUV spectrometer located at a right angle to the target surface as represented in figure [2.1]. In this chapter, the laser used to create the plasmas and the data collection and processing equipment will be described.
Figure [2.1]. The experimental apparatus used to measure spectral and time resolved data from the excited vapors.
SPECTRA-PHYSICS DCR-3 Nd:YAG LASER AND PDL-2 DYE LASER

The Spectra-Physics DCR-3 laser is designed to provide 8 ns, 1 J pulses at 0.5 to 10 Hz. This laser is based on a Q-switched resonator in which a 8 cm long neodymium doped YAG rod is pumped by two Xe flashlamps at up to 70 KJ per pulse. The oscillator uses a diffraction coupled resonator giving the output beam a characteristic doughnut shape. In the Q-switched mode, population is allowed to build up in the rod until saturation, after which an 8 kV pulse is applied across the KD*P crystal in the Pockel's cell causing a reduction in cavity losses due to the resulting polarization rotation. The energy is quickly extracted in an 8 ns pulse which is injected into a synchronously pumped amplifier, increasing the power from 200 mJ to 1100 mJ. A sample pulse of the laser is shown in figure [2.2].

For experiments requiring a dye laser to prepare the lower state of barium, a portion of the 1.06 μm radiation was frequency doubled using a Spectra-Physics HG-2 harmonic generator. The harmonic generator contained a KD*P crystal which could be angle tuned to generate the second harmonic at 532 nm. The green light was separated from the fundamental by using a pair of dichroic mirrors having R=95% in the green region and T=95% in the IR. Approximately 350 mJ of green light could be obtained through harmonic generation. The green light was used to pump a Spectra-Physics PDL-2 dye laser with LDS 795 dye for the barium intercombination line transfer experiments at 7911 Å.
Figure [2.2]. Typical temporal output of the Spectra-Physics DCR-3 Nd:YAG laser. The FWHM of the pulse is 10 ns.
Nd:YAG laser. The FWHM of the pulse is 10 ns.

The Spectra-Physics PDL-2 laser uses a side-pumped, grating tuned oscillator in conjunction with a preamplifier and an amplifier, as shown in figure [2.3]. Each beam splitter separated approximately 8% of the incident beam to pump the first two stages of the dye laser. The remaining energy was focused by a cylindrical lens into the final amplifier stage, into which the low power, grating tuned, beam was injected. Using the 350 mJ pump beam, 15 mJ of laser light at 791.1 nm could be obtained for an efficiency of approximately 5%. In order to calibrate the dye laser, spectra of the laser output as illustrated in figure [2.4] were taken with a monochromator to test both the linewidth and tunability of the dye laser. The monochromator's scale was corrected using a Cd lamp and used to tune the dye laser to the barium intercombination line at 7911 Å. The linewidth measured by the monochromator was 4 Å and corresponded to the instrument resolution for a slit width of 25 μm. The actual linewidth of the dye beam was probably close to the 0.5 cm\(^{-1}\) (0.3 Å) quoted by the manufacturer.

To allow time for the light from the dye laser to pump the intercombination line, the 1.06 μm beam used to produce the laser plasma had to be delayed with respect to the dye beam. Mirrors added 3 meters (9 ns) to the path length of the Nd:YAG beam to allow sufficient time for lasing to build up in the dye laser (5 ns) and to allow population to build up in the laser-designated level.

Radiation from the laser was focused onto a 2 mm thick tantalum target which was rotated during the experiments to
Figure [2.3]. Schematic showing the operation of the PDL-2 Dye Laser used to pump the barium vapor for laser-designated photoionization.
Figure [2.4] Sample scan showing the output of the dye laser as a function of wavelength. The linewidth shown corresponds to the resolution of the monochromator.
was AR coated for 1.06 μm radiation and used to focus the radiation onto the target. In order to measure the focal spot size, a razor blade was mounted on a translation stage and scanned through the focus. The transmitted energy was monitored using a Scientech energy meter. If the laser has an intensity in the focus equal to I(z) then the energy, E(z), transmitted as a function of the position of the razor blade in the focus is given by

\[ E(z) = \int_0^z I(z) \, dz \]

and therefore \( I(z) = \frac{dE(z)}{dz} \). A plot of the transmitted energy versus position is given in figure [2.5], along with the derivative \( dE(z)/dz \). A estimation of the diameter of the focus can be gained by measuring the half width of the \( dE(z)/dz \) curve. For the case shown, the diameter of the focal spot was 250 μm. For a typical beam of 800 mJ in a 10 ns pulse, the total fluence on the target was \( 2 \times 10^{11} \) W/cm².

**BARIUM HEATED CELL**

The barium heatpipe was configured as a six way cross made from SS316. The inside walls of the cell were lined with tantalum foil for better corrosion resistance against molten alkali and rare-earth alkali metals. Inside the foil were placed several layers of stainless steel mesh. The mesh served as a wick, using surface tension to draw the molten metals towards the hotter zones of the
Figure [2.5]. Graph depicting the transmitted intensity of the laser beam as a razor blade is moved through the focus. The focal diameter is measured as the FWHM of the dI/dz curve.
cell encouraging recirculation. The cell was initially loaded with 100 grams of barium and replenished with an additional 50 grams periodically. With the wicks present, it was possible to use the cell at temperatures of 1000 °C for 12 hours without having significant losses of barium in the heated zone. At temperatures above 1200 °C the vacuum integrity of the cell was lost due to structural failure and containment of the vapor was no longer possible. The temperature of the cell was maintained with ceramic heaters and resistive heaters made of Kanthal wire which could withstand temperatures of up to 1200 °C. The heaters could supply a maximum of 2.55 KW to the cell. In addition to heating the outside of the cell, the interior of the target rod was heated with a 40 W heater to prevent barium from condensing on the surface of the target. The temperature of the cell was closely monitored during the experiments to help determine vapor pressures and to protect against structural failure by using 20 chromel-alumel (Omega #XC-K-24) thermocouples to monitor the temperature at various places along the arms of the cell. At a temperature of 1000 °C on the surface of the cell, the vapor pressure inside the cell as measured using resonant absorption was typically 0.3 to 0.5 Torr barium. This indicates a temperature drop from the surface of the cell to the inside of the cell of $\Delta T = 260 \, ^\circ\text{C}$ as measured from the barium vapor pressure curve shown in figure [2.6].

The measurement of the vapor pressure inside the heated cell was made using the absorption width of a known barium resonance line at 553.5 nm. From the absorption width (equivalent width), it
Figure [2.6]. Barium vapor pressure as a function of temperature.

was possible to calculate the number of absorbers/unit area. By making an assumption for the vapor column length, it was possible to obtain the number density of ground state barium atoms and, hence, the pressure. In practice, these numbers have been found to be in good agreement with the known vapor pressure curves implying a uniform temperature both inside and outside the cell (for a detailed analysis see VAPOR PRESSURE MEASUREMENTS) [13].

HELIUM CELL

For experiments involving helium it was not necessary to use a heated cell since helium is a gas at room temperature. The cell used was also a stainless steel six way cross with its axes at right angles to one another. The cell could be filled with 0.1 millitorr to 1 atm of helium (99.9995% pure). Also constructed for use in the helium cell was a resonator equipped with broadband aluminum VUV mirrors (Acton type 1200, R=0.5") having reflectivities of up to 85% in the VUV. One mirror had a radius of curvature R = 0.5 m and was on a Pyrex substrate. Due to the poor transmissive qualities of Pyrex in the VUV, and the enhancement in solid angle obtained from using a curved mirror, the curved mirror was always used on the side opposite the spectrometer. The other mirror was a flat mirror mounted on a magnesium fluoride (MgF2) substrate having good transparency down to 115 nm.

VACUUM PUMPS

The pressure inside both the cell and the spectrometer were
controlled using a mechanical vacuum pump and a four inch diffusion pump equipped with a liquid nitrogen cold trap. By using these two pumps, it was possible to pump the barium cell down to pressures less than $5 \times 10^{-4}$ Torr. Buffer gases were fed simultaneously into each arm of the cell to preserve the heatpipe action of the cell, and could be monitored using a mechanical pressure gauge having a range of 0-50 Torr. To monitor the pressure limit of the diffusion pump, the top was fitted with a compression seal which held an ionization gauge. The region not covered by these two gauges was read using a resistive vacuum thermocouple gauge.

**DETECTION EQUIPMENT**

One end of the cell was attached to an Acton VM-502 scanning Vacuum Ultraviolet 0.2 meter spectrometer. The spectrometer consisted of an input slit and two output slits, chosen by use of a osmium coated diverter mirror. The grating of the spectrometer was also osmium coated to have a spectral range from 30 to 550 nm. The Acton VM-502 spectrometer uses an aberration corrected grating, having a blaze wavelength of 120 nm, 1200 grooves/mm, and a dispersion of 4 nm/mm. The reflectance of the grating at the 121.5 nm line in helium is specified by Acton to be approximately 85%. Because many of the measurements made were done below 100 nm, it was impossible to separate the environment of the spectrometer from the molten alkali metals. To protect the grating, it was necessary to pressurize the spectrometer with the buffer gas to a pressure equal to the buffer gas pressure in the cell, and to keep the
shutter closed whenever possible.

Fluorescence produced in the cell was filtered by the spectrometer and detected using a Hamamatsu 6199 photomultiplier tube. The tube had a ten stage dynode resistive network biased at 1100 volts which could amplify currents from the photocathode by $1.6 \times 10^7$. The photocathode was an S-11 photocathode sensitive to light from 300 to 650 nm and had a manufacturer specified quantum efficiency of 15% at the peak of the scintillator response. Since the photomultiplier tube was blind to the VUV radiation, a scintillator was used to convert the VUV photons into visible photons. The scintillator was made by spraying a saturated solution of sodium salicylate in methanol onto a Pyrex substrate which was placed directly in front of the photomultiplier tube. Sodium salicylate has a fluorescence time of 7-12 ns [14] and a quantum efficiency of approximately 65% in the VUV. The scintillator's spectral response is depicted in figure [2.7] along with the quantum efficiency of the photocathode.

Pulses from the photomultiplier tube could be analyzed in several fashions. The signal was sent to a boxcar integrator which sampled a portion of the pulse each time the laser fired, and added it to a running average. The laser also triggered the boxcar interface shown in figure [2.8] sending a data point to the computer representative of signal's average during the boxcar's gate. The beginning and end points of the scan were entered into the computer to scale the waveform. Further smoothing, data reduction routines, and fitting could be done with the boxcar's software. Signals from
Figure [2.7]. Scintillator fluorescence as a function of the wavelength. The fluorescence from the Na-Saly is sharply peaked at the maximum of the photocathode response.
Figure [2.8]. Timing and wiring showing the temporal relationships between the detection equipment and the measured signals.
the photomultiplier tube were also sent to a 400 MHz Tektronix (#11302) micro-channel plate enhanced oscilloscope which has resolution of up to 500 picoseconds per division. Enhancement of the oscilloscope image by a micro-channel plate made fast scans, normally difficult to see in real time at 2 Hz, visible at 500 picoseconds per division. Information on the oscilloscope was converted from an analog to a digital signal through the use of a digitizing CCD camera (Tektronix # DCS01) attached to the front of the oscilloscope screen. The CCD camera used a light trigger from the screen to begin its data acquisition. The CCD array was 512 x 512 bins which could be read in terms of their (x, y) coordinates. Each (x, y) pair on the CCD array corresponded to a point on the screen. Once the array was triggered, the computer read the (x, y) points on the CCD array and the associated charge, proportional to the screen intensity. Data reduction routines found the center of the trace and converted it into a waveform displayed on a computer monitor. The CCD camera and computer were able to average a number of shots, reducing the noise associated with single shots. The software for the CCD camera interface contained a number of data reduction routines for smoothing and subtraction of background light associated with the Ta plasma. The interface of the boxcar and oscilloscope to the computer allowed efficient storage and manipulation of time-resolved and spectral data from the VUV spectrometer.

VAPOR PRESSURE MEASUREMENTS

In all of the measurements taken, a precise determination of the
vapor pressure was needed for pressure calculations and to monitor depletion in the cell. The simplest way to measure the vapor pressure was to assume a uniform temperature across the cell and infer a vapor pressure from the known vapor pressure curves. Unfortunately, this does not take into account depletive effects that may lower the vapor pressure from its ideal value. A method that allowed measurement of the vapor pressure, without disturbing the vapor in the cell, was an absorption measurement. For determining the vapor pressure of barium, the resonance line at 553.5 nm was used. Since this line has a high cross section for absorption ($f=1.59$), it becomes optically thick at relatively low pressures (0.1 Torr), and an approximation for the equivalent width of the transition may be used. Secondly, since this line was in the visible region, a suitable broadband source for these measurements was a high intensity projection lamp.

For the measurement, a lamp was shined along the optical axis of the cell through the vapor column. A spectrometer was scanned from 550 to 555 nm and the signal monitored on a chart recorder. From the area of the absorption region and a given intensity the equivalent width can be measured as shown in figure [2.9]. For an optically thick sample, the expression for the equivalent width, $W_{eq}$, is given by [15]

$$w_{eq} = \sqrt{\frac{\pi e^{2} f_{i} k N \lambda \Gamma}{\epsilon_{0} mc}}$$

$f_{i}$ is the oscillator strength.
Figure [2.9]. Schematic representation showing the relationship between the equivalent width and the area of an absorption curve.
N is the density of the vapor
L is the vapor length
G is the linewidth of the transition
Therefore the number density times the length is
\[ N_L = \frac{5.66 \times 10^{11} \, W_{eq}^2 \, \text{cm}^{-1}}{f_{ik} \Gamma} \]
For the calculations of vapor pressure the medium is assumed to be Doppler broadened and homogeneously self-broadened. Since the cell is operated as a heatpipe, the pressure broadening due to buffer gas atoms is assumed to be small. For a typical temperature of 1300 K, the Doppler broadened width is
\[ \Gamma_{Dopp} = \sqrt{\frac{T(K)}{m(\text{au})} \frac{71.6 \, \text{cm}^{-1}}{\lambda(\text{Å})}} \]
which gives \( \Gamma_{Dopp} = 0.039 \, \text{cm}^{-1} \) while the self broadened width
\[ \Gamma_{self} = \sqrt{\frac{g_i}{g_k}} \frac{4 \pi e^2 f_{ik} N}{m \omega_0} \]
\[ = 4.548 \times 10^{-18} \, N \, \text{cm}^{-1} \]
g_i = 1
\( g_k = 3 \)
f_{ik} = 1.59
The Doppler broadened width is the dominant term for pressures less than about 0.1 Torr, while for pressures greater than 0.1 Torr the resonant self-broadening term is dominant. The heatpipe was operated at temperatures at which the vapor pressure was greater
than 0.1 Torr, subsequently the calculations for number density used the self-broadened width as the dominant term. Substitution for the constants in the equation, using the self-broadened term for $\Gamma$ and $L = 12$ cm, the expression for the number density as a function of equivalent width is given as

$$N^2 = 7.82 \times 10^{28} W_{eq}^2 = 8.07 \times 10^{13} W_{eq}$$

The pressure, in turn, can be calculated from the density by

$$P = \frac{760 \text{ (torr) } T(K) N(\text{cm}^{-3})}{273(K)L_0}$$

where $L_0$ is Lohschmidt's number $= 2.69 \times 10^{19}$ atom/cm$^{-3}$ STP. Using these numbers, the pressure calculated from the equivalent width for the 553.5 nm transition in barium is given as

$$P(\text{Torr}) = 8.36 \times 10^{-6} W_{eq}(\text{cm}^{-1}) T(K)$$

Due to the low vapor pressure of barium, only a fraction of a Torr pressure could be established in the heatpipe cell. Measurements of rubidium vapor pressure in a similar cell, however, shows the general utility of the absorption measurement technique. The results of these measurements are illustrated in figure [2.10]. The measurements indicate that the pressure measured by the absorption technique was accurate despite the fact that the temperature on the outside of the cell was probably higher than the temperature on the inside. The measured pressure also follows the theoretical vapor pressure curve well as the temperature is increased. The data also showed the limitations of this cell at 10 Torr.
Figure [2.10]. Vapor pressure curve and vapor pressure measurements using the resonant absorption technique for Rb in a heated cell.
rubidium, where the length of the cooling zone was not long enough to support heatpipe operation, and depletion occurred. A second source of inaccuracy in the measurements was the assumption that the vapor length was 10 cm. In reality, an equivalent width measurement only measures the number density multiplied by the length of the vapor column. The length of the vapor column changes, however, with increasing buffer gas pressure and tends to decrease the measured pressure when not taken into account.
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Chapter 3: Barium Experiments

INTRODUCTION

Recently, electron impact studies in the atomic species barium have shown a bright photoemission at 71.2 nm [16]. The 71.2 nm emission may be from a quasi-metastable state in the singly ionized barium atom, Ba(II), however, up to this point, this emission has not been identified. During the course of these preliminary investigations, another emission has been seen at 68.5 nm which may also be from a quasi-metastable state. It is the purpose of this work to provide tentative assignments for the barium emissions, and to provide an experimental means for their identification by using laser-designated photoionization to help confirm the upper and lower levels of the transitions. Once these levels have been identified, the suitability of the emissions as short wavelength sources will be investigated.

THEORY

Researchers at Stanford University have extensively investigated quasi-metastable states in alkali atoms [17]. An electron having an energy higher than the first ionization threshold will have a high probability for leaving the atom and becoming a free electron in a process known as autoionization. For some states, momentum conservation rules do not favor this form of decay. The increase in their autoionization times allows these highly excited levels to be seen radiatively. These levels, known as
quasi-metastable states, are therefore good laser candidates.

Recent experiments by Aleksakhin et al [18] have used intersecting atomic and electron beams to study the photoemission and threshold energies for various core-excited states in alkali and rare-earth alkali atoms. A collimated beam of barium atoms was intersected with a beam of electrons of known energy. Radiation from the excited atoms and ions was monitored by a spectrometer operating in the XUV from 50 to 90 nm. In barium, the first line to be seen is a strong emission at 71.2 nm which has a threshold for excitation of $23.3 \pm 0.5$ eV, but has not been identified. An additional unidentified line at 69.5 nm with an excitation threshold of 88.3 eV was also seen but not mentioned in later publications. The emission from the 71.2 nm line along with others were monitored as a function of the electron beam energy allowing the excitation functions to be measured. Other than the emission at 71.2 nm, strong resonant Ba(III) ion lines were also seen at 55.5 nm, 58.7 nm, 64.7 nm, 65.3 nm, and 74.3 nm. These lines and their identifications are summarized in table [3.1].

The transition at 71.2 nm seen by Aleksakhin may correspond to a quasi-metastable state in the Ba(II) ion. This is supported by the strong radiative behavior of the transition despite the fact it lies well above the second ionization threshold of the atom. Secondly, there is a strong correlation between the unidentified lines seen by Aleksakhin and quasi-metastable transitions previously identified by Mendelsohn et al at Stanford University [19]. The third piece of experimental evidence is the excitation function measured by
<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>Transition</th>
<th>$E_{\text{threshold}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>55.5</td>
<td>Ba (III) $5p^5 5d^3P_1 \rightarrow$ Ba(III) $5p^6 1S_0$</td>
<td>31.9 eV</td>
</tr>
<tr>
<td>58.7</td>
<td>Ba(III) $5p^5 6s^3D_1 \rightarrow$ Ba(III) $5p^6 1S_0$</td>
<td>34.2 eV</td>
</tr>
<tr>
<td>64.7</td>
<td>Ba(III)$5p^5 6s [3/2,1/2] \rightarrow$ Ba (III) $5p^6 1S_0$</td>
<td>34.4 eV</td>
</tr>
<tr>
<td>65.3</td>
<td>Ba(III) $5p^5 5d^3D_1 \rightarrow$ Ba(III) $5p^6 1S_0$</td>
<td>36.3 eV</td>
</tr>
<tr>
<td>71.2</td>
<td>unidentified</td>
<td>23.3 eV</td>
</tr>
<tr>
<td>74.3</td>
<td>Ba(III) $5p^5 5d^3P_1 \rightarrow$ Ba(III) $5p^6 1S_0$</td>
<td>37.5 eV</td>
</tr>
</tbody>
</table>

Table [3.1]. Transitions in barium in the region from 50-90 nm. From Aleksakhin et al 1977.
Aleksakhin for the 71.2 nm transition. The emission from the 71.2 nm line is shown as a function of energy in figure [3.1]. The excitation function for the 71.2 nm transition is strongly peaked, whereas the excitation function for the resonant transition to the ground state of the Ba(III) ion shows a broad continuum. The excitation function for the 71.2 nm line is similar to other excitation functions involving a quartet to doublet transition.

The question naturally arises, which quasi-metastable state might be responsible for this emission? From the measured threshold excitation energy, it is known that the radiating level lies approximately 23.3 eV above the ground state of the barium atom. If the transition created by the electron beam in Aleksakin's experiments is a quartet to doublet transition, then it is suspected that the emitting level is in the Ba(II) ion where the spin coupling leads to the formation of quartet states. A transition involving a 71.2 nm photon also indicates that the radiating level is 17.4 eV above the lower level. This places the lower level at 5.91 ± 0.5 eV above the ground state of the barium atom, or about 0.6 eV above the ground state of the Ba(II) ion, as depicted in figure [3.2]. The lower manifold of the Ba(II) ion is reasonably well understood and the placement of the lower level corresponds well with the 5p^{6}5d^{2}D_{3/2,1/2} level.

The interaction of an electron beam and an atomic beam will give rise to a number of final states. If an inner-shell ionization is to take place from the 5p^{6}6s^{2}1S_{0} ground state, the most likely are
Figure [3.1]. The excitation functions for the emissions in Ba at 71.2 nm and 74.3 nm. The strongly peaked function for the 71.2 nm emission suggests a quartet to doublet transition. From Aleksakhin et al, 1977.
Figure [3.2]. Energy level placement for the 71.2 nm emission in the Ba(II) ion having a threshold excitation of 23.3 eV.
those that remove a 5p electron, which has the highest cross section for ionization in the region from 20 eV - 75 eV. Since the emission from the 71.2 nm state is the first to be seen as the electron energy is increased, then it is reasonable to consider the lowest lying core-excited configurations: 5p^56s^2, 5p^56s6p, 5p^56s5d, and 5p^55d^2. The most likely transition of the four is the 5p^56s^2, however, this configuration has no quartet levels since two s electrons with opposite spins will fill the orbital. The next lowest lying core-excited states having quartet multiplicity are the 5p^56s6p, 5p^55d^2 and the 5p^56s5d. If the 5p^65d^2 D level is the lower level of the transition, the most likely transition would be one in which a core-excited electron fell back into the 5p shell, namely

\[ 5p^5nl5d \rightarrow 5p^65d + \text{hv} \]

Recalling that the lower level of the transition involves a 5d state and a filled p subshell, the most likely configurations are the 5p^56s5d and 5p^55d^2 since these transitions involve the decay of a 6s or 5d electron to fill the hole in the p subshell.

To evaluate the possibility of seeing either of these configurations in a radiative decay, one must consider the likelihood of producing these configurations from the ground state of the barium atom due to initial state configuration interaction or final state configuration interaction during the photoionization process. Mixing with the ground state 5p^66s^2 1S_0 configuration of the barium atom is allowed for the 5p^65d^2 1S_0 configuration favoring production of the 5p^55d^2 configuration. Mixing of the 5p^66s5d
$^3D_{1,2,3}$ state with the ground state is not allowed and production of this configuration from the ground state would be unlikely. The core-excited states can also be produced through coupling of the upper levels with the $5p^56s^2$ state. The high cross section for removal of a 5p electron makes $5p^56s^2$ easily obtainable from the ground state of the atom. Dirac-Fock codes predict that the $5p^56s5d$ will have greater coupling to $5p^56s^2$ than to $5p^55d^2$. In summary, coupling to the ground state favors the production of the $5p^55d^2$ state, while coupling to $5p^56s^2$ favors production of the $5p^56s5d$ state, and it is difficult to evaluate the relative strengths of these interactions in the production mechanism.

Corresponding to the $5p^56s5d$ configuration, there are two likely quasi-metastable states. These are the $^4P_{5/2}$ and the $^4F_{3/2}$ states [20]. Evidence from two electron autoionization studies [21] suggests that the $^4P_{5/2}$ level autoionizes to the ground state Ba(III) ion. The energy of this level based on this process is too low for the 71.2 nm emission threshold, and, since it has a strong autoionizing behavior, there is very little expected radiative yield. The remaining level for the transition is therefore the $5p^56s5d$ $^4F_{3/2}$. One reference [22] based on a calculation has tentatively assigned an eigenstate to the $^4F_{3/2}$ term which lies too low in energy to have a 71.2 nm emission to the $^2D$ level of the Ba(II) ion. This calculation is unpublished and therefore is difficult to evaluate in the context of this work.

Very little can be concluded about the upper and lower states of
the 71.2 nm or the observed 68.5 nm transition without some experimental data. The proposed experimental design to help identify the emissions in the barium system was a laser-produced plasma which could photoionize barium vapor contained in a heatpipe. If the emissions could be seen in the plasma, the next step was to introduce a dye laser beam into the cell to selectively place the ground state barium atoms into different states in the lower manifold. In particular, it was desirable to place a large number of the ground state barium atoms in a state whose electronic structure was similar to the upper level core-excited states. A laser-produced plasma would be introduced shortly after the lower level preparation to photoionize the excited atoms.

LASER-DESIGNATED PHOTOIONIZATION

Using an appropriately tuned dye laser, it is possible to put a portion of the ground state into an excited state in the lower manifold of an atom. The process is attractive in barium because a population in the $5p^6 6s5d$ $^3D$ level is metastable and takes a long time to decay to the ground state. In order for an electron to make the transition from the $^3D$ metastable to the $^1S$ ground states, it must change both its spin state and its orbital angular momentum such that

$$\Delta L = 2$$
$$\Delta S = 1$$

The quadrupole transition ($\Delta L = 2$) makes the relaxation to the ground state very slow and it takes place on a time scale of $10^{-3}$
seconds. This would allow sufficient time to photoionize the atoms with a laser-produced plasma after the atoms had been placed in the laser-designated level. Removal of an inner shell 5p electron from the 5p⁶6s⁵d configuration would result in 5p⁵6s⁵d, which is the same as one of the configurations of the proposed upper level of either the 71.2 nm or 68.5 nm transition.

Recent experiments by Carlsten et al [23] have attempted to place atoms in the 5p⁶6s⁵d ³D₁,₂,₃ levels. Using a pulsed dye laser having 1MW/cm² in a 30 ns pulse tuned to the intercombination line at 791.1 nm, Carlsten has achieved population densities in the ¹S₀, ³P₀,₁,₂ and ³D₁,₂,₃ levels in proportion to the degeneracies of the states (1:3:9). In Carlsten's experiments, the levels equilibrate according to their degeneracies in approximately 10⁻⁹ seconds. Once the dye laser pulse ends, the ³P levels relax into the ³D and ¹S levels with a relative branching ratio to the ³D level of 50%, placing the total number of atoms in the ³D level at approximately 80%. The relaxation process from the ³P level to the ³D level takes several milliseconds and was not practical for adaptation to the present experimental apparatus since only one laser was available to both produce the plasma and to pump the dye laser. Nevertheless, placing 50% of the ground state atoms in the ³D level should enhance the laser-produced plasma transfer to the upper levels having a 5p⁵6s⁵d configuration. Not all of the atoms which lose a p electron will populate the ⁴F₃/₂ term, but they should populate the different angular momentum states of the 5p⁵6s⁵d configuration
roughly according to the ratio of their degeneracies (shown in table [3.2]) leaving a approximately 4-5% in the $^{4}F_{3/2}$ term. In order to efficiently pump the upper level of the $5p^{5}6s5d$ transition, an effective means of photoionizing the $5p$ electron needs to be applied. As mentioned previously, a laser-produced plasma produces photons having energies in the 10-75 eV range, where the cross section for the photoionization of a $5p$ electron is highest.

**BARIUM PHOTOIONIZATION**

Laser produced plasmas produce soft x-rays whose energies typically lie in the region between 10 and 100 eV. For these energies, the photons have a high probability of removing a $5p$ electron from the barium atom. For the photoionization cross sections shown (figure [3.3]), a calculation was made to determine how many $5p$ electrons would be removed from the atom. In the simplest case, the number of ions produced through photoionization is given by [24]

$$N_{\text{ion}} = \frac{N_{\text{gnd}} \eta E_{\text{laser}}}{2.70 \ kT \ \pi d^{2}}$$

$N_{\text{gnd}}$ is the number of ground state atoms

$= 7.6 \times 10^{16} \ \text{cm}^{-3} \ (8 \ \text{torr})$

$\eta$ is the laser to soft x-ray conversion efficiency $= 10\%$

$kT$ is the temperature of the plasma $= 10 \ \text{eV}$

$d$ is the distance from the target $= 5 \ \text{mm}$
<table>
<thead>
<tr>
<th>Core configuration</th>
<th>L-S States</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>5p^5 6s5d</td>
<td>4F_{9/2,7/2,5/2,3/2}</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>4D_{7/2,5/2,3/2,1/2}</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>4P_{5/2,3/2,1/2}</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>2F_{7/2,5/2}</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>2D_{5/2,3/2}</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>2P_{3/2,1/2}</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 3.2. The L-S coupled configurations possible for the 5p^5 6s5d electronic configuration in Ba(II).
Figure [3.3]. Electron photoionization cross sections for barium. The probability for removal of a 5p electron is high for energies $E = 20-75$ eV.
\( \overline{\sigma}_1 \) is the spectrally averaged cross section given by
\[
\overline{\sigma}_1 = \frac{1}{\sqrt{2}} \int_0^\infty \sigma \frac{kT}{\hbar} \frac{x^2}{(e^x - 1)} \, dx
\]
\[x = \frac{\hbar \omega}{kT}\]

The volume illuminated by the plasma was assumed to be a 45° cone having a height \( d \). This integral was calculated numerically from the graph of the Bar(I) cross sections. The results are shown in table [3.3] for an incident laser energy of 750 mJ. The results of this calculation do not include the photoionization of the 5d electron due to a lack of reliable information concerning its cross sections. The cross sections for the 5d electron are not well understood, but they show a number of resonant structures near the peak photoionization cross section of the 5p electron. The photoionization of the 5d electron is expected to be on the same order as the photoionization of the 5p electron and will decrease the number of 5p electrons photoionized by approximately 50%.

From the results of the calculation, it is apparent that the dominant process will be the photoionization of a 5p electron which should enhance a transition from the \( 5p^56s5d \) configuration. If one assumes as in figure [3.4], that one has \( 7.6 \times 10^{16} \text{ cm}^{-3} \) atoms in the ground state, corresponding to a pressure of 8 torr, then the number of atoms that can be placed in the \( 3^D \) level of the ground state is
\[
N_{3D} = (0.5) (7.6 \times 10^{16}) \text{ cm}^{-3}
\]
\[
= 3.8 \times 10^{16} \text{ cm}^{-3}
\]
<table>
<thead>
<tr>
<th>Level</th>
<th>$\sigma_1 = \frac{1}{\sqrt{2\pi}} \int_0^\infty \sigma \left( \frac{kx}{\hbar} \right) \left( \frac{x^2}{e^x - 1} \right) dx$</th>
<th>$N_{ion} = \frac{N_g \eta E_{laser}}{2.7 kT \pi d^2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5p</td>
<td>$7.395 \times 10^{-18}$ cm$^2$</td>
<td>$6.2 \times 10^{15}$ cm$^{-3}$</td>
</tr>
<tr>
<td>6s</td>
<td>$4.588 \times 10^{-21}$ cm$^2$</td>
<td>$3.85 \times 10^{12}$ cm$^{-3}$</td>
</tr>
<tr>
<td>4d</td>
<td>$3.487 \times 10^{-20}$ cm$^2$</td>
<td>$2.92 \times 10^{13}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Total</td>
<td>$3.849 \times 10^{-20}$ cm$^2$</td>
<td>$3.23 \times 10^{13}$ cm$^{-3}$</td>
</tr>
</tbody>
</table>

Table [3.3]. Results of the photoionization calculations for barium.

The ground state barium density is $7.6 \times 10^{16}$ cm$^{-3}$. 
Figure [3.4] Energy level diagram for the excited states of barium with the laser-designated photoionization shown.
If these atoms are photoionized by a laser-produced plasma, then the number of atoms in the $5p^5 6s5d$ state of the ion will be

$$N = 3.1 \times 10^{15} \text{ cm}^{-3}.$$

If we assume that these electrons will populate the $5p^5 6s5d$ level roughly according to the degeneracies of the L-S coupled terms, then about 4% or

$$N_{4F_{3/2}} = 1.2 \times 10^{14} \text{ cm}^{-3}$$

will be in the desired upper level of the transition. Aleksakhin showed that the strongest emissions were in the cesium quartet followed by barium (71.2 nm) and calcium. From a large number of experiments done on the cesium quartet, the emission cross section from this transition is believed to be approximately $5 \times 10^{-14} \text{ cm}^2$ [25]. A reasonable number for the cross section for stimulated emission in the barium quartet is therefore $1 \times 10^{-14} \text{ cm}^2$. If we assume that the lower state of the transition is empty, the small signal gain,

$$I = I_0 e^{\alpha L}$$

-- on the barium transition for a path length of 1 cm should be $e^{1.2}$.

The photoionization of the $6s$ electrons from the laser-designated level is calculated to be smaller than the photoionization of the $5p$ electrons. Unfortunately, removal of a $6s$ electron places population in the lower level of the transition, $5p^6 5d^2 2D$, which could make establishing an inversion difficult. If the losses in the upper state due to autoionization make this type of laser unobtainable, then a storage density of $10^{13} \text{ cm}^{-3}$ should be suitable
for an anti-Stokes Raman laser provided appropriate energy levels can be identified.

**DYE LASER CONSIDERATIONS**

For the available dye laser energy, one concern was its ability to efficiently pump the vapor column in the region directly in front of the target. For an insufficient energy fluence, all of the dye laser energy would be absorbed before reaching the target area preventing proper laser-designation of the lower level in the interaction region. In the experiments by Carlsten, it was possible to use He pressure broadening to increase the linewidth of the intercombination transition to effectively use the energy in the relatively broad linewidth of the dye laser pulse. For the experiments in this work, which were performed in a heatpipe, the pressure of the buffer gas had to be kept low, and the linewidth is dominated by the Doppler broadened linewidth. The Doppler broadened linewidth is small, and it was necessary to consider how much energy could be placed inside the linewidth of the transition using the PDL-2 dye laser. If the barium is considered to be Doppler broadened, the width of the transition is

\[
\Delta \nu = \sqrt{\frac{T(K)}{M(au)}} \frac{71.6 \text{ cm}^{-1}}{\lambda(\text{Å})}
\]

\[T = 1300 \text{ K} \]
\[M = 137 \text{ au} \]
\[\lambda = 7911 \text{ Å} \]

therefore
\[ \Delta \nu = 0.03 \text{ cm}^{-1} \]

The bandwidth of the PDL-2 dye laser is specified at 0.2 cm\(^{-1}\) by Spectra-Physics. Under these conditions, the dye laser profile is approximately 10 times wider than the width of the transition. The energy needed to saturate the transition depends on the cross section for absorption. At the center of a Gaussian profile the absorption cross section is given by

\[
\sigma_{\text{abs}} = \frac{8.31 \times 10^{-13} f_{ik} \text{ cm}^2}{\Delta \nu \text{ (cm}^{-1}\text{)}} = 2.3 \times 10^{-13} \text{ cm}^2
\]

The saturation energy is given by

\[
E_{\text{sat}} = \frac{\hbar \omega}{\sigma_{\text{abs}}}
\]

For a 791.1 nm photon, the saturation energy is 1.1 \(\mu\text{J/cm}^2\). Since the dye laser has a linewidth that is roughly 10 times the linewidth of the transition, for a dye output of 15 mJ, approximately 10\%, or 1.5 mJ, falls within the linewidth of the 7911 Å transition. If one assumes that the dye laser beam must pass through 12 cm of barium vapor to reach the active volume, and that the pressure of the barium in the cell is 0.3 torr (1100 °C), then the number density of barium atoms in front of the active region is \(N = 2 \times 10^{15} \text{ cm}^{-3}\). The total number of absorbers in front of the target is therefore

\[
N_{\text{tot}} = N r^2 \pi l
\]

\[= 6.3 \times 10^{16} \text{ atoms} \]

\(r\) is the diameter of the dye beam = 5 mm
1 is the distance to the target = 12 cm.

The intensity of the transmitted light as function of length is proportional to \( \exp(-N\sigma l) \). Using the calculated numbers for the absorption cross section and total density, the intensity of the light at the target (\( l=12 \text{ cm} \)) is

\[
I = I_0 e^{-N\sigma l} = I_0 e^{-10^5}
\]

This implies that the dye beam will not have a good chance of reaching the active volume unless the linewidth of the dye laser is decreased, the linewidth of the barium transition is increased, or the size of the dye beam is decreased. The simplest method to use was the latter, and a focusing lens was used to decrease the size of the beam. Using the grating of the spectrometer as a mirror, it was possible to monitor transmission of the dye beam through the vapor with a photodiode. The dye beam was tuned to the intercombination line by scanning the dye beam and monitoring the intensity at the photodiode to detect the minimum value. Since much of the dye laser energy monitored was probably outside the bandwidth of the intercombination transition, it was difficult to determine how effectively the transition was saturated.

**EXPERIMENTAL APPROACH**

Initial experiments were performed to determine whether the 71.2 nm emission, reported by Aleksakhin, could be seen in a laser-produced plasma. Once the emission had been seen and
optimized with respect to the experimental parameters, a dye laser would be introduced to test whether or not the lower level preparation favored the 71.2 nm emission. If the lower level preparation to the 5p^6 6s5d level does not enhance the transition, different lower levels could be tested to see their effect on the radiative strength of the 71.2 nm radiation.

A valuable tool is the presence of barium ion lines near the transition which give a good calibration source as well as a measurement of whether the dye laser is tuned to the intercombination line. The transitions in the Ba(III) ion are shown in table [3.4] along with the expected effect on the transition when the lower level is excited to the 5p^6 6s5d 3D state. When the dye laser fills the 3D level, there will be an increase in the number of electrons in 5d orbitals, favoring the resonant ion transitions involving 5d electrons, namely the 74.3 nm and 65.3 nm lines. By monitoring the relative intensities of these lines with respect to the 64.7 nm line, it should be possible to gauge the effectiveness of the lower level preparation.

EXPERIMENTAL RESULTS

A) WITHOUT DYE LASER TRANSFER

The initial experiments focused on observing the resonant ionic transitions and the 71.2 nm transition in a laser-produced plasma without using the dye beam to prepare the lower state of the barium. The heatpipe cell was loaded with 100 grams of barium and heated to a temperature of 1050 °C. At this temperature, the corresponding
<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>Transition</th>
<th>Enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td>55.5</td>
<td>Ba (III) 5p⁵5d ³P₁ ---› Ba(III) 5p⁶ ¹S₀</td>
<td><strong>yes</strong>: 5d state</td>
</tr>
<tr>
<td>58.7</td>
<td>Ba(III) 5p⁵6s ³D₁ ---› Ba(III) 5p⁶ ¹S₀</td>
<td><strong>no</strong>: 6s state</td>
</tr>
<tr>
<td>64.7</td>
<td>Ba(III)5p⁵6s [3/2,1/2] ---› Ba (III) 5p⁶ ¹S₀</td>
<td><strong>no</strong>: 6s state</td>
</tr>
<tr>
<td>65.3</td>
<td>Ba(III) 5p⁵5d ³D₁ ---› Ba(III) 5p⁶ ¹S₀</td>
<td><strong>yes</strong>: 5d state</td>
</tr>
<tr>
<td>74.3</td>
<td>Ba(III) 5p⁵5d ³P₁ ---› Ba(III) 5p⁶ ¹S₀</td>
<td><strong>yes</strong>: 5d state</td>
</tr>
<tr>
<td>71.2</td>
<td>unidentified</td>
<td><strong>yes</strong>: if upper level 5p⁵6s5d or <strong>no</strong>: no 6s5d in upper level</td>
</tr>
<tr>
<td>68.5</td>
<td>unidentified</td>
<td></td>
</tr>
</tbody>
</table>

Table [3.4]  Resonant ionic transitions and their expected relative emissions after laser-designation of barium ground state to the 5p⁶6s5d ³D.
barium vapor pressure was measured to be 0.35 torr using the resonant absorption technique described earlier. The spectrometer was scanned at 40 Å/minute with the laser operating at 2 Hz. This corresponded to a collection efficiency of 3 samples/Å and significantly increased the signal-to-noise ratio. The boxcar average was set at 10 samples to further reduce the shot-to-shot noise. The distance from the target to the optical axis was varied from 3 mm to 15 mm. Due to the low pressures used in the cell, the distance from the optical axis to the target did not significantly effect the signal intensity, but did effect the amount of plasma light seen. The spectrometer's slits were opened to 100 μm so that the spectrometer's resolution was on the order of 4 Å.

A spectral scan from 640 Å to 750 Å of the barium vapor fluorescence is shown in figure [3.5]. In the scan the most prominent feature seen is the transition at 64.7 nm corresponding to the Ba(III) 5p⁵6s --> Ba(III) 5p⁶ ¹S₀. Small signals were also seen from the Ba(III) 5p⁵5d ³P --> Ba(III) 5p⁶ ¹S₀ at 74.3 nm. The other resonant ion line corresponding to a 5p⁵5d transition was too near the strong 64.7 nm line to be resolved, but its magnitude was expected to be comparable to the 5p⁵5d resonant ionic transition at 74.3 nm. Also shown in the scan is the 71.2 nm transition, and its magnitude was comparable to the 74.3 nm resonant ionic transition. Additional features were periodically seen at 68.5 nm and 69.5 nm, but it was not apparent from these scans whether the features seen at 69.5 nm and 68.5 nm were transitions with small radiative yields.
or were artifacts of the noise. These features were consistent enough, however, to investigate the effect of the dye laser preparation on their intensities. Additional spectral scans were taken at lower vapor pressures of 0.15 - 0.2 Torr due to failure of the first heatpipe at the extreme temperatures necessary to establish higher pressures. These scans, which are shown in figures [3.6-3.9] along with a list of identifications in table [3.5], encompassed a broader range of wavelengths from 50 nm to 400 nm. At these lower pressures, the Ba(III) transitions are no longer visible in comparison to the Ba(II) transitions. This suggests the need for a higher temperature barium heatpipe.
Figure [3.5]. Spectral scan without dye laser preparation of barium from 64 nm - 75 nm. The measured Ba vapor pressure was 0.35 Torr at $T = 1050 \, ^\circ \text{C}$. Spectrometer had slit width of 100 $\mu\text{m}$. 
Figure [3.6]. Barium scan for 0.2 Torr barium in the region from 50-143 nm. The temperature was 975 °C, slits were at 250 μm.
Figure [3.7]. Barium scan for 0.2 Torr barium in the region from 100-200 nm. The temperature was 975 °C, slits were at 250 μm.
Figure [3.8]. Barium scan for 0.2 Torr barium in the region from 200-300 nm. The temperature was 975 °C, slits were at 250 μm.
Figure [3.9]. Barium scan for 0.2 Torr barium in the region from 300-400 nm. The temperature was 975 °C, slits were at 250 μm.
<table>
<thead>
<tr>
<th>#</th>
<th>Ion</th>
<th>Transition</th>
<th>$\lambda_{th}$ (nm)</th>
<th>$\lambda_{meas}$ (nm)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>He$^+$</td>
<td>n=6 $\rightarrow$ 2</td>
<td>102.57</td>
<td>102.87</td>
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<td>He$^+$</td>
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<td>n= 4 $\rightarrow$ 2</td>
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<td>121.93</td>
</tr>
<tr>
<td>4</td>
<td>He$^+$</td>
<td>n= 3 $\rightarrow$ 2</td>
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<td>164.16</td>
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<tr>
<td>5</td>
<td>Ba$^+$</td>
<td>5p$^6$ (9d $\rightarrow$ 6p)</td>
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<td>205.67</td>
</tr>
<tr>
<td>6</td>
<td>Ba$^+$</td>
<td>5p$^6$ (8d $\rightarrow$ 6p)</td>
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<td>216.63</td>
</tr>
<tr>
<td>7</td>
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<tr>
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<td>223.44</td>
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<tr>
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<tr>
<td>13</td>
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<td>234.78</td>
</tr>
<tr>
<td>14</td>
<td>Ba$^+$</td>
<td>5p$^6$5d8p $\rightarrow$ 5p$^6$6s$^2$ (?)</td>
<td>243.3</td>
<td>243.1</td>
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<td>15</td>
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<td>5p$^6$5d12p $\rightarrow$ 5p$^6$6s$^2$ (?)</td>
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<td>247.63</td>
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<td>264.64</td>
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<td>277.12</td>
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<td>5p$^6$6s(7p $\rightarrow$ 6s)</td>
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<td>308.32</td>
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<td>389.22</td>
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<td>393.37</td>
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<td>391.39</td>
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<tr>
<td>25</td>
<td>Ba$^+$</td>
<td>5p$^6$6s(4f $\rightarrow$ 5d)</td>
<td>399.34</td>
<td>399.37</td>
</tr>
</tbody>
</table>

Table [3.5]. Summary of the lines and identifications observed in barium at a pressure of 0.2 Torr in the region from 50-400 nm. $\lambda_{th}$ is the accepted value, $\lambda_{meas}$ is the value taken from the scans in figures [3.6-3.9].
B) DYE LASER TRANSFER EXPERIMENTS

Once the dominant spectral features that appeared with no dye laser preparation of the lower level had been identified, it was possible to introduce the dye beam into the cell. The dye laser transfer measurements were made at the lower vapor pressures of approximately 0.2 Torr. The introduction of the dye laser beam into the cell produced an increase in the noise of the photomultiplier signal. Because of the increased noise, and the decrease in the Ba vapor pressure, it became more difficult to resolve the ion lines and the unidentified emissions seen in the earlier scans.

For a fixed spectrometer wavelength, the dye laser was scanned by hand allowing ten samples for every 0.16 Å. These scans are shown in figures [3.10-3.12] for the 67.4 nm, 65.3 nm, 68.5 nm, 71.2 nm, 72.5 nm, and 74.3 nm, along with their identifications. The background signal showed an increase as the dye laser wavelength approached resonance. To measure the amount of background signal enhancement at resonance, the dye laser was scanned through the intercombination transition while monitoring the intensity at 72.5 nm, where no spectral features were present. The spectrometer was then tuned to each of the known Ba(III) ion lines and the 71.2 nm and 68.5 nm lines and the dye laser experiment was repeated. The resonant ionic transition at 64.7 nm showed an increase similar to the increase seen at 72.5 nm, representative of background enhancement. The 71.2 nm transition did not show any enhancement other than the baseline increase, suggesting that the upper state of the 71.2 nm transition was not strongly coupled to the
Figure [3.10]. Dye laser scans of the 72.5 nm and 64.7 nm lines. The scan at 72.5 nm represents the enhancement of the background radiation at resonance. The resonant ionic transition at 64.7 nm shows an increase comparable to the background enhancement, and thus represents no real enhancement.
Figure [3.11]. Dye laser scans of the 71.2 nm and 65.3 nm lines. The 71.2 nm transition does not show any enhancement other than the background enhancement, while the 65.3 nm transition shows the expected increase due to dye laser preparation of the lower level.
Figure [3.12]. Dye laser scans of the 68.5 nm and 74.3 nm lines. The 68.5 nm transition shows an enhancement other than the background enhancement, as does the 74.3 nm transition.
the laser-designated state. The resonant ionic transitions at 65.3 nm and 74.3 nm which were expected to couple strongly to the laser-designated level did show an enhancement larger than the enhancement seen at 72.5 nm. The unidentified feature at 68.5 nm also showed an increase approximately equal to the increase seen in the ionic resonant transitions at 65.3 nm and 74.3 nm implying that the upper level of this transition was coupled to the laser-designated level. The additional increase in the resonant ionic transitions involving a $5p^55d$ upper level indicated that the dye laser transfer was at least partially successful.

DISCUSSION

Barium is a heavy (137 amu) atom, resulting in heavy coupling of configurations having different L-S coupled terms. In processes involving excitation of a core electron, neither the initial state or the final state is a pure L-S coupled state, and mixing between the L-S states will have an effect on the excitation function as well as the emissions. In particular, the coupling between the $5p^56s5d$, $5p^56s^2$, and $5p^55d^2$ core configurations in the Ba(II) ion will have an effect on the assignment of the upper level of a transition to a L-S coupled term. The coupling between the $5p^66s^2$, $5p^66s5d$, and $5p^65d^2$ core configurations in the initial state will also play an important role in the cross section for excitation to the upper level. To reevaluate the core-excited states based on the observed data, it was necessary to consider the spin-orbit mixing of the upper levels. To calculate the mixing between states, Dirac-Fock integrals may be solved for the
eigenvectors of the Ba(II) configurations. The energy eigenvectors are expressed in terms of how much of each L-S coupled basis state comprises the eigenvector. Table [3.6] is a list showing the eigenvectors for the Ba(II) ion [27]. The eigenvectors are listed along the uppermost row, while the given L-S coupled configurations are listed in the leftmost column. The square of the coefficient in the table may be used to estimate the percentage of a pure L-S coupled term that makes up a given eigenvector. The energies at the bottom of each column represent the difference between the eigenvector energy and the ground state of the Ba(II) ion. For example, eigenvector 1 has a high percentage of $5p^55d^24D_{3/2}$ and probably would be labeled using this L-S coupled state.

The reported data on the 71.2 nm emission and the preliminary results obtained during the course of this work may be summarized as follows:

1) The narrow excitation function of the transition suggests that the upper level is a quartet state in the Ba(II) ion.

2) The threshold excitation and the wavelength of the emission coincides with the lower level identification $5p^65d^22D$.

3) The identification of the lower level as $5p^65d$ makes a transition from an upper level having a core-excited configuration involving a 5d electron likely.

4) Low excitation threshold and relatively high radiative yield without dye laser preparation suggests that the state should have reasonable coupling to the ground state of the barium atom, or to an easily obtainable upper level such as $5p^56s$ and should be
### Table 36. Energy Levels and Mixing Coefficients for the Triple-Manifold m.D.–F.–al. J = \(\frac{3}{2}\) Ba II Calculation

<table>
<thead>
<tr>
<th>$LS$ state</th>
<th>1</th>
<th>2</th>
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<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5p^65d^4F^3$</td>
<td></td>
<td>0.0037</td>
<td>-0.0492</td>
<td>-0.3546</td>
<td>0.1415</td>
<td>0.0212</td>
<td>-0.4430</td>
<td>-0.6408</td>
<td>-0.0295</td>
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<td>$5p^55d^5$</td>
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<td>-0.0147</td>
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<td>-0.1407</td>
<td>0.0747</td>
<td>0.0317</td>
<td>-0.2528</td>
<td>0.1253</td>
<td>-0.2574</td>
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<tr>
<td>$(1P)^2P_0$</td>
<td></td>
<td>-0.0076</td>
<td>0.0413</td>
<td>0.4070</td>
<td>0.0458</td>
<td>0.0789</td>
<td>0.0287</td>
<td>-0.2896</td>
<td>0.6551</td>
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<td>$(1D)^2D_1$</td>
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<td>-0.0030</td>
<td>-0.0290</td>
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<td>0.2156</td>
<td>-0.4432</td>
<td>-0.0481</td>
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<td>$^4P_1$</td>
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<td>0.8895</td>
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<td>-0.2908</td>
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<td>$5p^55d^5(1S)^2$</td>
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<td>0.0359</td>
<td>-0.0074</td>
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<td>0.0360</td>
<td>0.1256</td>
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<tr>
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<td>0.1005</td>
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<td>0.0865</td>
<td>0.0511</td>
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<tr>
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<td>-0.3865</td>
<td>-0.5272</td>
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</table>

Energy/cm$^{-1}$†:

- 120 606
- 127 147
- 132 560
- 137 104
- 138 365
- 139 444
- 142 967
- 143 714
- 146 924

† Relative to single manifold m.D.–F. $5p^65s^2$ state.
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<th>level</th>
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<th>12</th>
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<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
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<td>$^{6p^5 6s^{1+}}_{1}F_4$</td>
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<td>0.1064</td>
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<td>-0.0280</td>
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<td>-0.0011</td>
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</tr>
<tr>
<td>$^{6p^5 5d^1 6s^1}<em>{1}(^{1}F</em>{1})F_4$</td>
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<td>0.0089</td>
<td>0.0207</td>
<td>-0.1037</td>
<td>-0.2337</td>
<td>0.5966</td>
<td>0.0475</td>
<td>0.1105</td>
<td>0.0332</td>
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<td>$^{6p^5 5d^1 6s^1}<em>{1}(^{3}F</em>{1})F_4$</td>
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<td>0.1154</td>
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</table>

Energy/cm$^{-1}$†

| 150 629 | 153 421 | 158 482 | 163 857 | 168 500 | 174 000 | 179 334 | 185 776 | 193 083 |

† Relative to single manifold m.D. - F. 6p$^5$ 6s$^1$ state.

Table 3.6

(Cont.)

Relative mixing coefficients for Ba($II$)
reasonably metastable against autoionization.

5) Preliminary dye laser preparation indicates that the upper level is not strongly coupled to the $5p^66s5d \; ^3D$ or $5p^66s6p \; ^3P$, both of which were populated by the dye laser pumping of the intercombination line.

From the available information it may be possible to tentatively associate the emission at 71.2 nm with and an eigenvector from the Dirac-Fock codes of reference [27]. The most likely assignment for this transition would be eigenvector 8, corresponding to a $5p^55d^2 \; ^4F_{3/2}$ L-S coupled state. This assignment agrees well with the data at this point in that:

1) This level should not be enhanced by dye laser preparation of the lower level. From the energy level placement of eigenvector 8, a radiative transition to the $^2D$ level of the Ba(II) ion would involve a 72.2 nm photon,

$$5p^55d^2 \; ^4F_{3/2} \rightarrow 5p^65d \; ^2D_{3/2,1/2} + 72.2 \text{ nm}$$

in good agreement with the 71.2 nm photon observed experimentally.

2) The level lies at a relatively low energy and is radiatively coupled to the $5p^55d \; ^2D_{3/2,1/2}$ lower level. The transition involves a relaxation of the 5d electron to fill the p shell and the transition is an allowed dipole transition($\Delta J=0$, $\Delta L=1$).

3) The state satisfies the rules for quasi-metastability, and couples to the ground state via the $5p^65d^2$ configuration. Spin-orbit coupling will mix the $5p^65d^2 \; ^1S_0$ term with the ground state $5p^66s^2$
$^1S_0$ ($\Delta L=1$, $\Delta J=0$) and production to the upper level should be possible without dye laser preparation.

A similar treatment may be done for the transition at 68.5 nm which did show enhancement when the dye laser prepared the lower level. It is much harder to place this level because there is no information available for its threshold excitation energy. From this work:

1) The 68.5 nm transition is enhanced when the dye laser places a population in the $5p^66s5d \, ^3D$ or the $5p^66s6p \, ^3P$ lower level, indicating that the upper level should be coupled to these configurations.

2) The radiative decay was not as bright as the decay for the 71.2 nm transition without the dye laser preparation suggesting that the mixing with the ground state barium configuration is small.

Based on these observations, the 68.5 nm emission has been tentatively associated with eigenvector 11, which would be labeled as the $5p^56s5d \, ^4F_{3/2}$ configuration. This eigenvector can decay to the $^2D$ level of the ion through a relaxation of the 6s electron to fill the $p$ subshell with the emission of a 67.5 nm photon

$$5p^56s5d \, ^4F_{3/2} \rightarrow 5p^65d \, ^2D_{3/2,1/2} + 67.5 \, \text{nm}$$

also in reasonable agreement with the 68.5 nm photon experimentally observed. This configuration is not coupled to the ground state of the atom, but could be produced through final state configuration interaction to the $5p^56s^2$ configuration and the $5p^56s5d$ configuration. Furthermore, it should be enhanced by dye
laser preparation of the lower level. In addition, the absorption spectrum of Ba(I) reveals a strong absorption near 69 nm [28]. The inability to resolve the 68.5 nm line in the scans done without dye laser preparation at 0.35 torr barium may have been caused by trapping of the transition by the ground state barium atoms. The ability to detect this transition at lower pressures using the dye laser preparation may have been the result of fewer absorbing atoms in the heated zone or a decrease in the number of ground state barium atoms as a result of the dye laser transfer.

At this point, however, the identifications presented here are tenuous, and a higher temperature cell needs to be constructed capable of sustaining vapor pressures of 10-20 torr (T>1350 K). In addition, the power of the dye laser needs to be increased to effectively pump the increased number of atoms in front of the target.

FUTURE EXPERIMENTS

Future experiments in the barium system will continue these measurements with an emphasis on the identification of the 71.2 nm and possibly the 68.5 nm transition. Methods for selectively placing the barium atoms in a lower level favorable to the production of the 71.2 nm transition based on these identifications are also being considered. The primary consideration before continuing these experiments is the construction of a high temperature cell able to support pressures of up to 10 torr barium (1300 C). The material considerations for this cell dictates the use of molybdenum. The
oxidation of molybdenum at high temperatures requires the molybdenum cell to be kept in an oxygen-free atmosphere during heating. Heaters will also have to made of a high temperature refractory metal, in this case tantalum due to its availability in wire form and its resistive qualities. Once a high temperature heatpipe is constructed, it should be feasible to bring the 71.2 nm transition out of the noise and initiate a dye laser transfer. The increase in the number of barium atoms present also will require more dye laser energy to pump the vapor column. For further enhancement of the 68.5 nm line, the commercially available dyes do not cover the region around 790 nm very well, the best dyes having only 5-10% efficiency. A titanium sapphire laser may be a suitable alternative for pumping the 7911 Å intercombination line.
Chapter 4: Helium Experiments

INTRODUCTION

With the current interest in fusion processes, the development of a laser in the He(II) ion would be of interest due to its isoelectronic structure to hydrogen. In the He(II) ion there are a number of transitions in the VUV that would appear at first glance to be good candidates for inversion (figure [4.1]). These transitions lie at 121.5 nm and 164.0 nm resulting from a change in the principal quantum number of the He(II) ion from the n= 4 -> 2 and from the n= 3 -> 2 states, respectively. The natural lifetimes calculated for the states in table [4.1] indicate that the lifetime of the n=2 state is much shorter than either the n=3 or the n=4 state. This implies that if good pumping to the upper levels can be achieved, the two states should invert themselves with respect to the n=2 state after a sufficient time has passed. These lifetimes do not take into account the effect of resonant trapping on the calculated lifetime of the lower state. If there are enough n=1 He(II) states present, the photon emitted by the n=2 -> n=1 transition will be reabsorbed by the n=1 ions as shown in figure [4.2] resulting in an effective increase in the lifetime of the n=2 state. Even at very low pressures, this effect is drastic enough to increase the lifetime of the n=2 state so that it is greater than the lifetime of either the n=3 or n=4 state.
Figure [4.1]. Transitions among the principle quantum numbers in the He(II) ion. The lifetimes at the left are the total lifetimes for the indicated level. Transition wavelengths are given in table [4.1].
Table [4.1]. Transitions among the principle quantum numbers of the He(II) ion. Indicated are the degeneracies of each level, the transition wavelength, the spontaneous emission coefficient, and the lifetime.

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<th>i</th>
<th>k</th>
<th>g&lt;sub&gt;i&lt;/sub&gt;</th>
<th>g&lt;sub&gt;k&lt;/sub&gt;</th>
<th>wavelength (nm)</th>
<th>f&lt;sub&gt;ki&lt;/sub&gt;</th>
<th>A&lt;sub&gt;ki&lt;/sub&gt; (1/s)</th>
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Figure [4.2]. Resonant trapping may increase the apparent lifetime of the n=2 state by reabsorbing photons from an n=2-->1 transition.
THEORY

When the soft x-rays from a laser-produced plasma photoionizes an inner-shell electron, one or more of the remaining electrons may be excited as a result of the perturbation in a process known as shake-up. After photoionization, the remaining electron will not be as efficiently screened from the charge of the nucleus and will want to assume a tighter orbital. The remaining electron may not always assume the ground state, however, and may end up in an excited state, depending on the time behavior of the perturbation, the spatial overlap of the different orbitals, and the energy of the incident photon. The shake-up process for helium is depicted in figure [4.3]. Recently, shake-up experiments performed in helium by Silfvast et al [29] have reported gain at 164 nm using the He(II) n=3-->2 transition. The approach used by Silfvast is similar to the system described in this work. Silfvast used soft x-rays from a laser-produced plasma created by a 70 picosecond 25 mJ Nd:YAG laser to pump a 1 cm length of He gas at a pressure of 50 Torr. The intensity of the fluorescence at 164 nm was monitored when a VUV broadband mirror was inserted into the cavity. From the ratio of the intensity with the mirror versus the intensity without the mirror, Silfvast calculated the gain length product (gL). Using this technique, gains of 0.7-0.9 cm\(^{-1}\) were observed [30]. The gain observed by Silfvast was at a helium pressure of 50 Torr where the calculated trapping is expected to make the lifetime of the n=2 state much longer than the lifetime of the n=3 state preventing inversion.
Figure [4.3]. In a process known as shake-up, photoionization of an electron from neutral helium may cause the remaining electron to assume a number of different orbitals in the He(II) ion.
Silfvast proposed that the mechanism by which the lifetime of the \( n=2 \) state was decreased may have been the photoionization of neutral He atoms by the photons from the \( n=2 \rightarrow 1 \) transition. When the \( 2 \rightarrow 1 \) photons ionize a ground state He(I) atom, the photons cannot be reabsorbed by a He(II) ground state ion to the \( n=2 \) state. As the lifetime of the \( n=2 \) state approaches the natural lifetime, the \( n=3 \) and \( n=4 \) states can be inverted with respect to the \( n=2 \) state.

To apply the results of Silfvast's experiments to the emission at 121.5 nm, it is necessary to calculate numbers corresponding to the \( n=4 \rightarrow 2 \) transition. The order in which this work addresses the computations is first to calculate the number of He (II) \( n=4 \) ions produced by shake-up. Once the threshold inversion density necessary is calculated for a given resonator, the percentage of ground state atoms that will populate the \( n=4 \) level after photoionization will determine the He pressure. The threshold inversion density can be obtained from the known losses in the resonator cavity and the cross section for stimulated emission. The calculated population density in the \( n=1 \) He(II) ion can be used to estimate the effective trapping of the He(II) \( n=2 \) state as a function of the He(II) ion number density and size of the excited volume.

PHOTOIONIZATION AND SHAKE-UP IN HELIUM

Calculations similar to the ones performed for Ba were done in He to determine the number of excited ionic states that would be produced in a He gas illuminated by soft x-rays from a laser-produced plasma. These calculations only considered the
populations as a result of direct excitation and did not include the effects of recombination on the upper level populations due to the low pressures ( ~ 1 Torr ) of these experiments. Calculations for the number of ions produced are recorded in table [4.2] for a ground state density \( N_g = 10^{17} \text{ cm}^{-3} \), \( E=800 \text{ mJ} \), \( \eta = 10\% \), \( d=1 \text{ cm} \) from the optical axis and \( kT=5 \text{ eV} - 20 \text{ eV} \).

The shake-up ratios can also be used to estimate the number of excited states following photoionization. These ratios reflect the asymptotic behavior of the cross sections as the energy is increased. The shake-up ratios reported in [31] are

\[
\begin{align*}
n=1 & \quad 93.98\% \\
n=2 & \quad 1.18-5.05\% \\
n=3 & \quad 0.29-0.62\% \\
n=4 & \quad 0.12-0.20\%
\end{align*}
\]

Both the photoionization calculations and the shake-up ratios scale according to the ground state density and determination of the threshold inversion density should define the threshold ground state density needed for inversion of the \( n=4 \) state with respect to the \( n=2 \) state.

**THRESHOLD INVERSION DENSITY**

At the minimum inversion threshold between the \( n=4 \) and \( n=2 \) states, the gain in the resonator is equal to the mirror losses in the resonator cavity. This result is only applicable for a cw pumping mechanism. For the more general case where there is a pulsed pumping source, the gain is dependent upon the photon lifetime and
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<td>1.1 x 10(^{12})</td>
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Table [4.2]. Results for the photoionization calculations in helium. The ground state density is \(10^{17}\) cm\(^{-3}\), \(E = 800\) mJ, \(\eta = 10\%\), and \(d = 1\) cm from the optical axis. All numbers are in cm\(^{-3}\).
the gain lifetime [32]. For the small resonator and highly reflective mirrors used for these experiments, the threshold inversion density is adequately described by the cw formula. The mirrors used for these experiments were Al coated broadband mirrors (Acton #1200) with approximately 80% reflectivity at 121.5 nm. Setting the gain equal to the cavity losses yields

$$\frac{1}{2l} \ln \left( \frac{1}{R_1 R_2} \right) = \Delta N \sigma_{se}(\nu)$$

$R_1, R_2$ are the reflectivities of the mirrors = 0.8

$l$ is the length of the cavity = 3 cm

$\Delta N$ is the threshold inversion density

$\sigma_{se}$ is the cross section for stimulated emission

The cross section for stimulated emission at the center of a Gaussian lineshape is given as

$$\sigma_{se} = \left( 8.31 \times 10^{-13} \frac{f_{ik}}{\Delta \nu} \right) \text{ cm}^2$$

$\Delta \nu$ is the Doppler broadened width of the transition

$$\Delta \nu = \sqrt{\frac{T(K)}{M(\text{au})}} \frac{71.6}{\lambda(\text{Å})} \text{ cm}^{-1}$$

$$\sigma_{se} = 5.1 \times 10^{-14} \text{ cm}^2$$

for $M = 4$ (au), $\lambda = 121.5$ nm, and $T = 293$ K. Solving the loss equation for $\Delta N$ using the calculated linewidth and the stimulated emission cross section yields

$$\Delta N = \frac{1}{2l \sigma_{se}} \ln \left[ \left( R_1 R_2 \right)^{-1} \right]$$

$$= 1.458 \times 10^{12} \text{ cm}^{-3}$$

The results of a photoionization calculation predicts that 0.04% of the
photoionized He ions will populate the n=4 state while shake-up predicts that 0.2% will populate the n=4 state. Making use of the threshold inversion density and that the plasma is 1% ionized, the neutral He density required for inversion is

$$N_{\text{He}} = (0.73 - 3.64) \times 10^{17} \text{ cm}^{-3}$$

$$= 2.3 - 11.3 \text{ Torr He (300 K)}$$

These two numbers provide a lower bound for the number of neutral helium atoms needed to invert the n=4 level with respect to the n=2 level.

**RESONANCE TRAPPING**

The inherent problem when considering a laser in the helium ion is resonant trapping by the ground state ions. Up to 98% of the photoionized ions are in the ground state and these are responsible for the absorptive effects that increase the lifetime of the upper states. The apparent increase in the lifetime of a state depends on the absorption cross section for a resonant photon, and its ability to escape the excited volume without reabsorption. From these observations, the trapping coefficient, $g$, should depend on the size of the excited volume and the resonant absorption length [33],

$$L = \frac{1}{k_0}$$

$$k_0 = \frac{\lambda^3 g_i/g_k N}{8 \pi^{3/2} \tau v_0}$$

$g_i$ and $g_k$ are the relative degeneracies for each level.
$\lambda$ is the transition wavelength in Å

$\tau$ is the natural lifetime of the upper level

$N$ is the number density of the lower state

$v_0$ is the thermal velocity of an electron

The amount by which the ground state ions increase the apparent lifetime of the upper levels is given by trapping coefficient $g$, where the apparent lifetime $\tau'$ is related to the untrapped lifetime, $\tau$ by

$$\tau' = \frac{\tau}{g}$$

For a long right cylinder whose radius is $R$, the trapping coefficient may be obtained from [34]

$$g = \frac{1.6}{k_0 R [\pi \ln(k_0 R)]^{1/2}}$$

For a number density $N = 7.3 \times 10^{14}$ cm$^{-3}$ corresponding to the number density in the He(II) $n=1$ state at the threshold for inversion, and a radius $R$ equal to 1 cm, the calculated trapping coefficient $g$ for the $n = 2$ level is approximately $10^{-4}$ implying an increase in the apparent lifetime of $10^4$.

The equation for the trapping coefficient reveals that the trapping can also be reduced through a decrease in the dimensions of the excited volume. Relationships between the size of the excited region and the trapping coefficient can be derived for a number of different size cylinders. A family of curves is shown for cylinders having $R = 1$ cm, 1 mm, 100 µm and 10 µm in figure [4.4]. The
Figure [4.4]. Trapping coefficient as a function of n=1 He(II) density and cylinder dimension R. The volume is assumed to be a long right cylinder whose radius is much smaller than its length.
natural lifetime of the n=2 level is 0.1329 ns, while the natural lifetime of the n=4 state is 2.09 ns. There exists a critical trapping coefficient for which the lifetime of the n=4 state is equal to the n=2 lifetime, viz.,

\[
\frac{0.1329 \text{ ns}}{\varepsilon_{\text{crit}}} = 2.09 \text{ ns}
\]

\[
\frac{1}{\varepsilon_{\text{crit}}} = 15.7
\]

The intersection of the critical trapping coefficient and the critical density for gain should give the approximate size of the physical system one can expect to see gain in. From figure [4.4], the minimum radius for which the lifetime of the n=4 state is equal to the n=2 state is 200 μm. It is possible to approach these dimensions using a capillary array. Soda lime glass tubes can be fabricated 50 μm in diameter and impressed into a disk up to 5 mm in thickness. A capillary array has the advantage of small individual dimensions but a reasonable total volume.

**EXPERIMENTAL PROCEDURE.**

Measurements of the fluorescent intensity and the decay times were taken from oscilloscope traces that were the average of 40 single shot measurements. The spectrometer was kept at a fixed wavelength and had a slit width of 500 μm. The averaged traces were obtained and stored via the CCD camera for pressures ranging between 0.5 and 10 Torr and energies on the target of 133 mJ - 684
mJ. Figure [4.5] shows a typical pulse shapes for the 121.5 nm, 164 nm, and 468.5 nm lines at 0.5 Torr He and 688 mJ incident laser energy. The averaged traces were measured for the decay times and the peak intensity and plotted as a function of energy and pressure for each transition. The results of these measurements are shown in figures [4.6-4.9]. The measurements of the fluorescence decay times as a function of pressure did not show any decrease that would expected with a decrease in the trapping of the n=2 level. A measurement of the plasma emission time reveals that the emission from the plasma is much longer than expected from a 10 ns pulse on a tantalum target. The FWHM of the plasma emission is 32 ns (figure [4.10]) which may contribute to the length of the emissions by continual pumping to the upper levels. In addition, all of the lifetimes measured for the transitions at 121.5 nm, 164.0 nm, and 468.5 nm were on the order of the plasma emission time.

Once the relative intensities were measured, a resonator as in figure [4.11] was introduced into the system having broadband VUV mirrors to see the relative effect on the intensities previously measured. In the tests to see inversion, one expects that there should be a significant increase in the intensity of the radiation with the VUV mirrors relative to the radiation intensity without the VUV mirrors. A second parameter indicating gain the system would be an exponential increase in the intensity as a function of the excited length.
Figure [4.5]. Oscilloscope traces for the 121.5 nm, 164 nm, and 468.5 nm lines at 0.5 Torr He. The traces are the average of 40 single shots at 688 mJ incident energy. The spectrometer's slits were 500 μm.
Figure [4.6]. Peak intensity measured from the average of 40 single shots versus the incident energy for the 121.5 nm transition. The He pressure was 0.5 Torr. Traces shown are with a VUV resonator (upper curve) and without a VUV resonator (lower curve).
Figure [4.7]. Peak intensity versus He pressure for the 121.5 nm transition measured from the average of 40 single shots. The incident energy was 688 mJ. Traces shown are with a VUV resonator (upper curve) and without a VUV resonator (lower curve).
Figure [4.8]. Peak intensity versus He pressure for the 164 nm transition measured from the averaged of 40 single shots. The incident energy was 688 mJ.
Figure [4.9]. Peak intensity versus pressure for the 468.5 nm transition measured from the averaged of 40 single shots. The incident energy was 688 mJ. Lower pressures showed depletion of 468.5 nm transition.
Figure [4.10]. Oscilloscope trace showing the temporal behavior of the plasma emission in vacuum at 60 nm. The trace is the average of 40 single shot measurements.
Figure [4.11]. VUV resonator used to measure relative intensities and decay times for the transitions at 121.5 nm, 164 nm, and 468 nm.
SOLID ANGLE ENHANCEMENT

The back mirror used for the resonator had a curvature of 0.5 m. The curvature of the mirror and its reflectivity was expected to enhance the solid angle seen by the spectrometer. To account for the enhancement of signal, a calculation was done to see what signal increase could be expected with the mirror in the resonator. The resonator along with the lengths measured for the experiment is depicted in figure [4.12]. The spectrometer has a f-number f/4.5 which for 500 μm slits gave an angular acceptance of 6.3 degrees. The distance from the slits to the edge of the excited volume was measured to be 11.7 cm. The radius of the mirrors was 12 mm. The volume seen by the spectrometer without the back mirror present is the volume of a truncated cone whose height is the distance between the mirrors. The angle of the truncated cone in the excited region is determined by the aperture between the spectrometer and the first mirror, and was calculated to be 2.9°. The excited volume is written as

\[ V_1 = \frac{1}{3} \pi d (r_1^2 + r_2^2 + 2r_1r_2) \]

d is the distance between the mirrors

\[ r_{1,2} \] is the radius of the cone at each mirror

For the resonator used \( d = 3.6 \text{ cm} \), \( r_1 = 0.6 \text{ cm} \) \( r_2 = 0.62 \text{ cm} \) and the volume is

\[ V_1 = 4.2 \text{ cm}^3 \]

Similarly, the volume that will be reflected by the curved mirror can be calculated. The angle of the truncated cone is increased to 4.43°
Figure [4.12]. Dimensions used to calculate the solid angle enhancement created by the back mirror of the VUV resonator.
by the curvature of the mirror. \( r_1 = 0.6 \text{ cm}, \ r_2 = 0.88 \text{ cm} \) and
\[ V_2 = 5.00 \text{ cm}^3 \]
The reflectivity of the mirror will decrease the intensity from \( V_2 \) by 0.8, therefore the relative enhancement expected by the addition of the VUV mirror is
\[ \text{RE} = 0.8(5.0) / 4.2 = 0.95 \]
In measurements taken at a broad range of pressures, the enhancement was never more than \( \text{RE} = 0.5 \). To estimate the magnitude of the solid angle enhancement from the experimental observations, the enhancement of the 468.5 nm line was used. From the graphs of \( R \) for 468.5 (figure [4.16], p. 104), the asymptotic value for the enhancement seen experimentally was
\[ \text{RE} = 0.1 - 0.2 \]
The enhancement is dependent on the reflectivity of the mirror and it is possible that during the course of the measurements, the reflectivity of the mirror decreased due to the observed coating of the mirror surface by tantalum products.

**DISCUSSION**

The relative enhancement for the three transitions is shown in figures [4.13-4.16] where the relative enhancement is defined to be
\[ R = \left( \frac{I_2}{I_1} \right) \]

\( I_1 \) is the peak intensity without the mirror present
\( I_2 \) is the peak intensity with the mirror in place
Figure [4.13]. $R$, the ratio of peak intensities versus incident energy measured from the averages of 40 single shots for the 121.5 nm transition at 0.5 Torr He.
Figure [4.14]. R versus He pressure measured from the averages of 40 single shots for the 121.5 nm transition at 688 mJ incident energy.
Figure [4.15]. R versus He pressure measured from the average of 40 single shots for the 164 nm transition at 688 mJ incident energy.
Figure [4.16]. R versus He pressure for the 468.5 nm transition measured from the average of 40 single shots at 688 mJ incident energy.
The relative enhancement of the 121.5 nm radiation at 0.5 Torr was accompanied by a depletion in the 468.5 nm radiation in the low pressure regions as shown in figures [4.13, 4.16]. Depletion of the radiative yield from the 468.5 nm line was observed in 4 of 5 measurements made at 0.5 Torr He and 688 mJ incident energy as represented in figure [4.17]. The enhancement of the 121.5 nm transition may have been an indication of gain since the 121.5 nm and the 468.5 nm transitions have the same upper level and gain on the 121.5 nm line would decrease the yield from the 468.5 nm line. The enhancement of the 121.5 nm radiation increased as the pressure decreased and increased as the energy on the target was increased. The 164 nm transition also showed a relative increase as the pressure decreased, which may indicate that the n=2 level was trapping radiation from these transitions at higher pressures.

There are a number of explanations that might account for the increase in the intensity of the 121.5 nm line with decreasing pressure. The increase in R may be the result of solid angle enhancement not seen at higher pressures due to the trapping of the 121.5 nm radiation. It is possible that trapping of the radiation from the n= 4-->2 transition made the vapor opaque to the 121.5 nm radiation at higher pressures so that the solid angle enhancement is seen only at pressures where the absorption length is significantly larger. If the n=2 state is trapped at higher pressures, then the radiation at 164 nm should show an increase similar to the one seen in the 121.5 nm radiation, which proved to be the case. Resonant trapping by the n=2 level does not, however, adequately explain why
Figure [4.17]. Oscilloscope traces showing the depletion observed on the 468.5 nm line at 0.5 torr He, 688 mJ incident energy. In 4 of 5 cases, the fluorescent intensity measured with the VUV resonator was approximately equal to the intensity measured without the resonator. The lack of any enhancement indicates depletion of the 468.5 nm transition.
the 468.5 nm transition was depleted at low pressures when a resonator was used. Deterioration of the mirrors during the course of the measurements would not account for this effect since measurements made with and without the mirror were taken in the same order so that any reduction in the reflectivity due to blow-off products from the target occurring with a decrease in pressure would have a similar effect on all of the transitions.

The depletion seen on the 468.5 nm transition at 0.5 Torr He may be due to an increase in the stimulated emission rate to the n=2 level. Without any inversion, the branching ratios of the n=4-->3,2,1 states can be calculated from the spontaneous emission coefficients. For a population in the n=4 level, 29.8% is expected to decay to the n=3 level, and 27.7% to the n=2 level. Making use of the experimentally observed enhancement of 0.2 with no gain present, then the 468.5 nm transition experienced a decrease in its branching ratio of 16.7% when depletion occurred. Similarly, an enhancement of R=1.43 for the 121.5 nm line implies an increase of 19% in the branching ratio to the n=2 state. If the increase in the branching ratio is due to an increase in the stimulated emission coefficient, it is possible to calculate the stimulated emission coefficient for the 121.5 nm transition. The sum of the branching ratios must equal unity

$$BR_{121} + BR_{468} + BR_{24} = 1$$

The ratio of the new branching ratio to the old branching ratio is 1.19, therefore

$$\frac{B_{121}}{A_{468} + A_{24} + B_{121}} \times \frac{A_{468} + A_{24} + A_{121}}{A_{121}} = 1.19$$
B is the combined coefficient for stimulated and spontaneous emission.

A is the coefficient for spontaneous emission.

Using the values from table [4.1] for the spontaneous emission coefficients, \( B_{121} \) can be solved for analytically

\[
B_{121} = 1.67 \times 10^8 \text{ s}^{-1}
\]

The depletion of the yield from the 468.5 nm transition can also be used to estimate \( B_{121} \). The 468.5 nm transition is depleted by 16.7%, therefore

\[
\frac{A_{468}}{A_{468} + A_{24} + B_{121}} \times \frac{A_{468} + A_{24} + A_{121}}{A_{121}} = 0.83
\]

Solving once again for \( B_{121} \) yields

\[
B_{121} = 2.26 \times 10^8 \text{ s}^{-1}
\]

The reasonable agreement of the two calculations for the emission coefficient seems to indicate that the depletion seen in the 468.5 nm transition is correlated to the fluorescence increase in the emission of the 121.5 nm transition in a manner that is consistent with gain.

To estimate the amount of possible gain for a certain a ratio of intensities, the following approximation was used. The intensity of the radiation without the mirror in place is \( I_1 \). The mirror will increase the signal due to feedback and small signal gain so that \( R = (I_1/I_2) \) is given by

\[
R = \frac{\alpha [\exp(gL) - 1]}{gL}
\]

g is the small signal gain.
L is the length of the gain region.

\( \alpha \) is the amount of enhancement without any gain

As discussed previously, \( \alpha \) was determined experimentally to be 1.1 - 1.2. Using \( \alpha = 1.2 \), a plot was made of the dependence of the gain length product on the ratio of intensities with and without the mirror for the 121.5 nm transition. The graph along with the measured gain length product is shown in figure [4.18]. These measurements indicate a gain of approximately 0.22 cm\(^{-1}\) for \( R=1.35 \) and a 1 cm length.

**FUTURE EXPERIMENTS**

There are two alternatives that have been considered to reduce the effects of trapping in the helium system. The first of these is a helium jet which reduces the trapping volume by limiting the size of the excited region. A second alternative that will be tested soon is the use of a capillary array. The capillary array uses a number of small (50 \( \mu \)m) tubes fused together into a disk. The capillary array has a number of very small excited regions which can all contribute to a reasonably large total volume.
Figure [4.18]. Calculated gain length product for the VUV resonator used for He measurements. The estimated enhancement is 1.2 due to the presence of the back mirror.
Chapter 5: Summary

The focus of this work has been the spectroscopy of core-excited and ionic levels of atomic systems for the development of short wavelength laser sources which operate in the VUV/XUV. To date two such systems have been proposed and preliminary investigations have been done in each.

Using laser-produced plasmas as an excitation source, an experimental apparatus has been designed to study the fluorescence from excited helium and barium. The soft x-rays from a laser-produced plasma efficiently photoionizes core electrons allowing the excited ionic states of barium and helium to be studied.

Preliminary investigations in barium have shown the usefulness of laser-designated photoionization as a diagnostic tool for studying core-excited states. The preliminary experiments provided a tentative identification of a previously unidentified 71.2 nm emission. Laser-designated photoionization may have also revealed other previously unknown core-excited transitions in the XUV, and based on the current theoretical and experimental information, a tentative identification has also been made for the 68.5 nm transition. Both identifications are in good agreement with the theoretical information available at this time.

Initial studies of the He(II) ion have made progress understanding resonant trapping in the system. Low pressure measurements in the helium system showed selective enhancement of the 121.5 nm and 164 nm transitions along with a decrease in the
emission from the 468 nm line when a VUV resonator was inserted into the excited volume in a manner consistent with gain.

Laser-designated photoionization will continue to be used as a tool to try and confirm the tentative identifications of the 71.2 nm and 68.5 nm lines in the Ba(II) ion. A high temperature heatpipe which can withstand the temperatures necessary to achieve 10 Torr barium vapor is currently being designed to increase the number of ground state barium atoms and, consequently, the efficiency of the lower level preparation.

Future experiments in helium will continue to investigate the enhancement observed on the ionic transitions at 121.5 nm and 164 nm. Novel geometries are being considered to limit the size of the excited volume, decreasing the trapping effects. The prospect of using capillary arrays as a means of achieving the small volumes necessary to overcome resonant trapping appear promising. In addition, a jet of helium may also be able to approach the dimensions needed to invert the populations in the n= 3,4 states with respect to the n=2 state.
REFERENCES


[34] T. Holstein, Physical Review 83(6), 1159 (1951).