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PHOTOEXCITATION OF CESIUM THROUGH DISSOCIATIVE STATES OF THE CESIUM DIMER

by

C. WESLEY WALTER

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

MASTER OF ARTS

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September, 1986
ABSTRACT

Photoexcitation of Cesium through
Dissociative States of the Cesium Dimer

by

C. Wesley Walter

The two-photon excitation of cesium to high-n Rydberg levels through resonant dissociative states of the dimer is investigated over the wavelength range 6000-5900Å. Highly vibrationally excited $^1\Sigma_g^+$ ground state molecules are excited to the continuum of $^1\Pi_u$ bound states which dissociate to give 5D atoms. The 5D atoms are subsequently photoexcited to high-n Rydberg states which are detected by selective field ionization techniques. Series corresponding to both (5D→nF) and (5D→nP) transitions with components up to n=150 were observed. The photoexcitation process appears to be very efficient and produces copious quantities of Cs Rydberg atoms.
ACKNOWLEDGEMENTS

It is my pleasure to acknowledge and thank the people who have contributed to this research. First, thanks must go to my advisor, Professor Barry Dunning, who has led our research group with both direction and insight. Dr. Ken Smith has provided many useful suggestions, as well as the guidance of his extensive experimental experience. In addition, two former graduate students have made essential contributions to this work. Dr. Byron Zollars has advanced the research projects in this laboratory in too many ways to even begin to enumerate - his contributions are greatly appreciated. Dr. Gary McMillian is responsible for much of the initial investigation of the two-step photoexcitation process, as well as the design of the ramp digitizer.

I would also like to thank my fellow graduate students, Chris Johnson and Alex Kalamidas, for keeping the machine running smoothly and for the many late night data-taking sessions we shared.

Finally, I would like to thank my family for their loving support and encouragement throughout both my undergraduate and graduate educations.

This research was supported by the National Science Foundation and the Robert A. Welch Foundation.
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I. Introduction

I.A. Overview

Serendipity - *n*: the gift of finding valuable things not sought for.

This thesis reports the observation and investigation of a two-step process for exciting high-n alkali Rydberg atoms in which a dissociating state of the dimer forms a resonant intermediate step. Serendipity played a major role in the origin of this research. The photoexcitation mechanism was first observed in this laboratory while studying collision processes using rubidium Rydberg atoms excited by direct two-photon absorption from the atomic ground state. During the course of these studies, Rydberg atom production was unexpectedly observed at a laser frequency adjacent to that for Rb(56D). This unexpected Rydberg atom was subsequently identified as Cs(37F) arising from a very small cesium impurity in the rubidium metal. The excitation mechanism was determined to be a two-step process: single photon excitation of a Cs$_2$ dimer to a continuum molecular state which subsequently dissociates into a ground state atom and an atom in a low-lying excited (5D) state followed by absorption of a second photon of the same wavelength by the 5D atom leading to excitation of a high-n Rydberg atom. Only the serendipitous arrangement of energy levels in Rb, Cs, and Cs$_2$, coupled with the fortunate contamination of the rubidium metal, permitted the excitation to be observed in the dye laser frequency range under study and led to the research presented here.

The thesis begins with a brief review of the general properties of Rydberg atoms, followed by a description of the experimental apparatus. The results of the research will then be discussed, starting with a brief
chronological account of the observation of the two-step photoexcitation process in this lab and proceeding to an analysis of some of the interesting aspects of the process.

I.B. Review of Properties of Rydberg Atoms

Atoms in which one electron is excited to a state of high principal quantum number \( n \) are known as Rydberg atoms. Rydberg atoms exhibit many properties that differ from those of ground or low-lying excited atoms. These properties make the Rydberg atom both an unusual occupant of interstellar space and a useful tool in the laboratory.

Perhaps the most striking property of the Rydberg atom is its size. Since atomic radii increase as \( n^2 \), Rydberg atoms are enormous on the atomic physics scale. While a ground state atom has a radius of \( \sim 1\text{Å} \), a Rydberg atom with \( n=100 \) has a radius of \( \sim 5000\text{Å} \). The highly excited electron is so far away from the ionic core, consisting of the nucleus and inner shell electrons, that it may be pictured classically as an electron orbiting a point-like positive charge. Because of the large orbital radius, the Rydberg electron experiences an almost purely Coulombic potential. For this reason, Rydberg atoms exhibit very similar properties regardless of the elemental species.

Since the Rydberg electron orbits far from the ionic core, it is obviously weakly bound. In a Coulomb field, the potential energy is proportional to the inverse of the radius, therefore the binding energy of the Rydberg electron scales as \( n^{-2} \). Typical binding energies are only a few millielectronvolts, indicating that Rydberg atoms are very fragile. At high \( n \) the energy levels become very closely spaced which, combined with the large size, suggests that small perturbations may significantly affect the
atom. Indeed, weak electric or magnetic fields, interactions with background blackbody radiation, and collisions with thermal molecules can cause either state-changing or ionization of a Rydberg atom.

The energy levels of a Rydberg atom are given by

\[ E_{n,l} = -\frac{1}{2(n-\delta_l)^2} \]

where \( \delta_l \) is the quantum defect and the quantity \( n-\delta_l \) is known as the effective quantum number, \( n_{\text{eff}} \). The quantum defect, which is a function of the angular momentum, results from the finite extent of the core ion. The Rydberg electron penetrates the inner core to a greater extent at low \( l \), making the screening of the nuclear charge by the inner electrons less complete, and thus leading to a higher binding energy. Since the quantum defect is related to \( l \) and the properties of the core, it provides a qualitative measure of how much the Rydberg state of a particular species differs from the corresponding state of hydrogen.

Although Rydberg atoms are large and fragile, they have very long radiative lifetimes in the absence of external perturbations. The natural lifetime scales approximately as \( n^3 \), with typical lifetimes ranging from \( \sim 1 \mu \text{sec} \) at \( n=10 \) up to \( \sim 1 \text{msec} \) at \( n=100 \). The long lifetime of the excited state permits the study of reaction processes on a time scale feasible in the laboratory.
II. Experimental Apparatus and Procedure

II.A. Apparatus

The apparatus used in these experiments is shown schematically in figure 1. Briefly, a collimated beam of alkali monomers and dimers, produced by effusive flow from an oven, traverses an interaction region defined by two parallel fine mesh grids. At the center of the interaction region the alkali beam is intersected at right angles by the focused output of a tunable dye laser. The excited states and ions thus produced are detected by either time-of-flight mass spectrometry or selective field ionization techniques.

II.A.1. Vacuum system and TIC

The experimental apparatus is contained in a two chamber vacuum system maintained at high vacuum by oil diffusion pumps. The alkali oven is mounted in the source chamber which is separated from the main chamber by a beam-collimating aperture. Typical background pressures are $\leq 1 \times 10^{-7}$ torr in the main chamber and roughly 5 times higher in the source chamber.

The excitation and interaction region is defined by two planar, parallel fine copper mesh grids mounted in a chassis called the total ion collector (TIC). The grids control the electric field in the interaction region and can have DC or pulsed voltages applied as required by the experiment. In addition, the TIC houses an ion drift region and a particle detector. The drift region is a metal tube with biasable grids on both ends, allowing for field-free drift of ions during time-of-flight mass spectrometry. A Johnston MM-1 particle multiplier serves as the charged particle detector.
Figure 1. Schematic diagram of the apparatus.
II.A.2. Production of excited states

a) Alkali beam

Most experimental research on Rydberg atoms involves alkali metal atoms. The alkalis are a natural choice due to their simple electronic configuration consisting of an ns electron outside a closed rare gas-like core. Furthermore, the relatively small amount of energy (2-5eV) required to promote their valence electron to a highly excited state allows state-selective optical excitation with presently available dye lasers.

In the present work rubidium or cesium beams are produced by effusion from a heated two-stage oven. The body of the oven provides a reservoir for the alkali metal and the nose contains a 0.5mm diameter hole which serves as the exit aperture for the alkali beam. The atoms or molecules which escape through the nose hole are collimated by a 1mm x 1.5mm aperture giving a full-angle divergence of approximately 2°. Operating temperatures are dictated by the vapor pressure of the particular metal in use and are typically ~220°C for Rb and ~200°C for Cs. The nose is maintained 20 degrees hotter than the body to prevent clogging.

After the alkali beam traverses the interaction region, it impinges on a hot-wire detector which allows the beam flux to be determined. The detector consists of a tungsten filament (5 mil diameter) stretched across a frame by stainless steel springs which is resistively heated to approximately 1400°C and biased to permit only positive ions to escape. The positive ion current leaving the filament is measured by a picoammeter. The beam density can then be calculated using the relation

\[ p = I/(\eta q A V) \]

where I is the current leaving the wire, q is the charge of an ion, A is the
active area of the wire, \( v \) is the average velocity of an atom in the beam, and \( \eta \) is the ionization efficiency of the filament. The ionization efficiency, as calculated using the modified Saha-Langmuir equation\(^2\), is \( \sim 95\% \) for Rb and \( 100\% \) for Cs atoms on tungsten at the operating temperature of \( 1400^\circ \text{C} \). The resultant measured beam density in the interaction region is approximately \( 1 \times 10^9 \, \text{cm}^{-3} \). This measured value is in reasonable agreement with calculations made on the assumption that there is an effusive flow from the oven, i.e. the particle flux leaving the oven is proportional to \( \sin \theta \), where \( \theta \) is the angle from the beam axis.

The fraction of diatomic molecules in the beam can be calculated from the ratio of monomer to dimer vapor pressures at the operating temperature of the oven. The values of these parameters\(^3\) yield a dimer fraction of \( \sim 0.2\% \) for cesium at \( 200^\circ \text{C} \) leading to a dimer density of \( \sim 2 \times 10^6 \, \text{cm}^{-3} \) in the interaction region. However, the dimer fraction in the beam is possibly higher than in the oven due to dimerization during the expansion of atoms as they leave the nose aperture. The fractional dimer density increases strongly with temperature due to the higher probability of dimer-forming three-body collisions.

b) Laser system

The laser system used in this work is a Coherent Radiation model 699-21 actively stabilized, single frequency ring dye laser pumped by a Coherent Innova 20-UV argon ion laser. The frequency range over which the ring laser will operate is primarily determined by the particular dye in use. For the present work Rhodamine 6G chloride, with a gain region extending from approximately 570nm to 610nm, is employed.
The frequency of the dye laser can be tuned over large ranges by a three plate birefringent filter or scanned over short ranges (up to 30GHz) with a galvo-driven Brewster plate. Short range scanning may be accomplished either manually or under computer control. By electronically locking the laser frequency to an external temperature-controlled reference interferometer, short-term frequency jitter is minimized. The resultant bandwidth of the laser is typically about 250kHz and the long-term frequency drift is ~50MHz/hour.

The continuous wave output of the dye laser can be modulated by a fast Pockels cell coupled with a linear polarizer to provide light pulses of from 0.5μsec to several μsec duration at repetition rates up to 50kHz.

High power densities are necessary to accomplish two-photon excitation of a Rydberg state. The power output of the dye laser is typically 1watt single frequency with an input pump laser power of 9watts. The power density is enhanced by tightly focusing the laser beam using a short (7cm) focal length lens. The resultant beam waist is ~5μm and lies at the center of the interaction region. In this manner, sufficient power densities are achieved to observe multiphoton events such as two-photon resonant photoionization of diatomic molecules and two-photon resonant three photon ionization of ground state alkali atoms.

II.B. Rydberg Atom Detection

In this work, Rydberg atoms are detected by selective field ionization (SFI). In this technique a ramped electric field is used to ionize the excited atoms and the liberated electrons are detected by a multiplier. A second technique, time-of-flight mass spectrometry (TOFMS), is employed to identify the ion species resulting from field ionization. Procedurally the
two techniques are similar, but they provide very different information. We will begin with a discussion of TOFMS, then consider SFI, and finally describe the electronics necessary for Rydberg atom detection.

II.B.1. TOFMS

TOFMS provides identification of the ion species present in the interaction region. The technique is based on the separation of ions of different mass by their flight time after acceleration through a small potential difference. Since lighter ions acquire a greater velocity than heavy ions, they are thus detected sooner. The theory of our TOFMS technique has been discussed elsewhere and we will be concerned only with the experimental details in this discussion.

After laser excitation, ions are extracted from the interaction region by a small, \( \sim 200\text{v/cm} \), electric field. The ions are then accelerated through a potential difference of \( \sim 500\text{v} \) and into a field-free drift region approximately 15cm in length. This drift time allows the different species to separate by mass due to their varying velocities. The ions are subsequently detected by a particle multiplier and the arrival times are recorded. The extraction and acceleration voltages are chosen to provide maximum temporal focusing of ions whose initial positions are at different points within the interaction region.

The time required for an ion of particular mass to traverse the flight path is easily calculable. However, it is more difficult to invert the equations of motion in order to derive the mass of the ion from its known flight time. In order to change the signal as a function of arrival time to signal as a function of mass, the flight time is calculated for a range of masses and an nth order polynomial is fit to the mass as a function of time.
This polynomial allows the conversion of the arrival time spectrum to a mass spectrum. The resolution of the present TOFMS system is sufficient to distinguish adjacent masses up to 100amu.

II.B.2 SFI

One of the most common techniques used for detection of Rydberg atoms is selective field ionization (SFI)\textsuperscript{5} in which the excited atoms are ionized by an increasing electric field and the liberated electrons are subsequently detected. The electric field at which ionization occurs is characteristic of the Rydberg state, thus measurements of the ionization signal as a function of electric field can be used to determine the Rydberg population and state distribution present in the interaction region prior to application of the field. However, the interpretation of SFI data requires a detailed understanding of the atom’s path to ionization.

The response of an excited atom to an electric field gives rise to the Stark effect, a shift in electron energy levels that is a function of the applied field. As the field is increased, the energy level shifts increase leading to avoided crossings of Stark levels associated with different $n$ manifolds, as illustrated in figure 2. Atoms may pass to ionization along two distinct paths\textsuperscript{6}: adiabatic passage in which the atom evolves adiabatically at avoided crossings of Stark states, successively changing character on the path to ionization; or diabatic passage in which the atom remains in its original Stark state until it is ionized. Although the details of the two paths are important for a quantitative analysis of SFI data, for our purposes it is sufficient to note that diabatic ionization occurs at an electric field strength roughly twice as great as that for adiabatic ionization.
Figure 2. Stark manifolds for $m = 0, 8 \leq n \leq 11$. The dashed line paths represent adiabatic passage, while the heavy solid curve corresponds to diabatic passage.
Experimentally, the SFI technique proceeds as follows. After laser excitation, a negative going high-voltage ramp is applied to one grid of the interaction region, while the second grid remains at ground. The electric field increases from 0-2000v/cm in \(\sim 1\mu\text{sec}\), sufficient to adiabatically ionize Rydberg atoms with \(n\) above 20. After ionization, the liberated electron is accelerated to a particle detector and the arrival time relative to the onset of the ionizing ramp is recorded. The high-voltage ramp is subsequently digitized (see section II.C.) and the field ionization signal is displayed as a function of electric field strength.

II.B.3. Electronics

Typical times between excitation and detection in Rydberg atom studies are a few microseconds, and the TOFMS and SFI techniques require nanosecond timing resolution. Thus, it is evident that fairly sophisticated electronics must be employed to provide the necessary accuracy in timing.

A block diagram of the electronics is shown in figure 3, and the experimental procedure is as follows. A master oscillator, operating at 20kHz, triggers an electro-optic modulator to produce a short laser pulse and simultaneously starts a computer-controlled delay. After this delay, which is typically a few microseconds, the extraction voltage ramp generator is triggered and one of two time-to-digital converters (TDCs) is started. For SFI, a multi-channel analyzer (MCA) with a resolution of 1nsec over a 1\mu\text{sec} active window is used. The TOFMS technique requires less timing resolution over a longer time range, therefore a quad-event timer (QET) which can measure intervals up to 20\mu\text{sec} with a resolution of 10nsec is employed. The extraction voltage serves to accelerate either the liberated electrons or ions to a Johnston MM-1 particle multiplier. The
amplified MM-1 pulse provides the stop signal for the TDC which registers the arrival time referenced to the beginning of the extraction ramp. The arrival time spectrum is then stored by an LSI 11/23 computer interfaced to the TDC through a CAMAC instrument crate.

Figure 3. Electronics block diagram.
II.C. Ramp Digitizer

As noted previously, the interpretation of SFI data relies on an accurate knowledge of the time dependence of the ionizing field produced by a high-voltage ramp. The voltage ramp used typically slews to 2000 volts in 1 μsec at a repetition frequency of 20 kHz. In order to characterize the ramp, we have developed a computer-controlled apparatus to measure, with high resolution, the time dependence of fast, repetitive high-voltage ramps.

The present apparatus is shown schematically in figure 4. The operating sequence begins when the master pulse generator triggers the high-voltage ramp generator and simultaneously starts a time-to-digital converter (TDC). The voltage ramp is input to the primary circuit board where it is attenuated by a factor of ~1000 by a frequency-compensated resistive voltage divider. The output of the divider is buffered by a high-speed, unity-gain amplifier and is fed to one input of a fast comparator. The second input to the comparator is a reference voltage supplied by a 12-bit digital-to-analog converter (DAC) which is set under computer control. When the ramp voltage at the output of the buffer amplifier exceeds the reference voltage the comparator output switches, thereby stopping the TDC. The computer then reads and records the output of the TDC thereby obtaining the time interval between the onset of the ramp and the time it reaches a specified voltage, taking into account the attenuation by the voltage divider. At each DAC setting a total of ~250 separate measurements of the time interval are accumulated, whereupon a statistical average is taken and stored. The DAC setting is then incremented and the entire process repeated. Measurements are taken at a total of ~200 DAC settings chosen to encompass the range of voltages associated with the
ramp. The data stored in the computer thus provides a detailed picture of the time development of the voltage ramp.

A polynomial is then fit to the data to obtain a mathematical description of the ramp for use in generating SFI profiles as a function of electric field strength. A sample voltage ramp map and the SFI profile obtained using this ramp is shown in figure 5.

The primary circuit board is a double-sided printed circuit board with one side serving as a ground plane. This construction is necessary to provide good ground return paths and short leads for the fast signals used.

One particularly critical component of the present apparatus is the voltage divider which must have low noise and a voltage division ratio that is independent of both frequency and temperature. The divider is constructed of Caddock precision film resistors that are non-inductive and that have low effective capacitance and good thermal stability. To make the voltage divider operation independent of frequency, the ratio of the capacitances $C_1$ and $C_2$ must be the inverse of the ratio of the resistances $R_1$ and $R_2$ (see figure 4). In practice, it was observed that the effective capacitance of the input resistor $R_1$ was so small that it was difficult to obtain frequency compensation by adjustment of the output capacitor $C_2$. A small capacitance was therefore added in parallel with $R_1$. This was accomplished by leaving a small strip of copper on the board connected to the input terminal of $R_1$ and running parallel to the resistor, as illustrated in the inset of figure 4. This circuit board capacitor was adjusted by physical removal of part of the copper strip until frequency compensation could be readily obtained with a 500pf ceramic trimmer capacitor $C_2$ in parallel with $R_2$. 
Figure 4. Schematic diagram of the high-voltage ramp digitizer.
Figure 5. Conversion of SFI data. (a) Ionization signal vs. time; (b) Map of the high-voltage ramp; (c) Signal vs. electric field.
In order to set $C_2$, high-voltage pulses were applied at the input to the divider while simultaneously monitoring the input waveform and the output waveform of the buffer amplifier using a fast oscilloscope. $C_2$ was then adjusted to obtain optimal matching of the input and output waveforms for a wide range of input pulse risetimes.

Once the voltage divider has been properly adjusted, the division ratio must be accurately determined. To calibrate the present device a range of DAC settings are selected and the corresponding DC input voltages required to switch the comparator are measured. In this manner the input voltage corresponding to each DAC setting is determined. This calibration technique has the advantage that any small DC offsets in the buffer amplifier, comparator, or DAC are automatically compensated. The DC calibration of the division ratio is reasonable because of the high speed of the buffer amplifier and comparator. To test the AC behavior of the voltage divider and buffer amplifier, a sine wave was applied to the input and the relative amplitudes of the input signal and output of the buffer amplifier determined by use of a phase sensitive detector. Measurements at frequencies over the range 100Hz to 250kHz showed that the ratio of output to input voltages varied by at most 1% over this frequency interval. A further confirmation of the adequacy of the present voltage divider for our purposes is provided by Fourier analysis of the voltage ramps typically employed, which have no significant frequency components above ~3MHz. The uncertainty in the measured voltages introduced by use of the DC calibration procedure is estimated to be $\leq 3\%$.

Propagation and switching delays are measured by injecting a fast pulse at the input of the buffer amplifier and observing the delay between
the time that this pulse reaches the threshold set by the DAC and the output pulse to the TDC. This time delay, which is only a few nanoseconds, is corrected for when determining the time-dependence of the voltage ramp. The ramp mapper and ion detection delays are included in a timing offset when displaying SFI profiles as a function of electric field strength.
III. Results

This section provides a chronological history of the observation and investigation of two-step photoexcitation of cesium Rydberg atoms through dissociative states of the dimer in our laboratory. It is intended to give the reader a feel for the experimental tools which were employed as well as an insight into the discovery process.

III.A. Observation of Anomalous Features

The excitation of Cs atoms to Rydberg states by means of dissociating states of Cs$_2$ was first observed in this lab as two unexpected features in a laser scan near 5943Å undertaken to investigate production of rubidium Rydberg atoms. Figure 6 shows this scan in which the frequency of the dye laser was stepped in 2MHz increments over a range of 8GHz and the electron signal produced by SFI was recorded at each frequency setting. The figure thus represents Rydberg atom production as a function of exciting laser frequency. The four high, sharp peaks correspond to two-photon excitation of rubidium atoms to 56D states from the ground state. The narrow width of these features results from the small effective Doppler width obtained by transverse beam excitation. In addition to these expected peaks, a small bump of 1GHz width is noticeable approximately 2.5GHz lower in frequency than the first Rb(56D) peak, while a second 1GHz wide bump lies between the second and third rubidium peaks.

Although the bumps represent only a small increase in the SFI signal, the anomalous features were consistently observed in scans performed in two different Rydberg apparatuses and over a range of days. The reproducibility of the scan profiles indicated that the signal enhancement was not a spurious effect.
Figure 6. (a) Laser scan near 5943Å showing Rb(56D) Rydberg states and unexpected features; (b) 10x magnification. Oven temperature = 200°C.
II.B. Identification as a Rydberg State

The first step in identifying the anomalous features was to determine the source of the enhanced signal — whether free photo-electrons or electrons liberated by field ionization of Rydberg atoms were responsible. For this purpose an SFI study was undertaken, as discussed in section II.B.2. The SFI profile obtained with the dye laser frequency tuned to the center of the left feature in the Rb(56D) scan, is displayed in figure 7. The peak at \(~170\text{v/cm}\) corresponds to the adiabatic ionization\(^6\) of an excited state with \(n_{\text{eff}} \approx 37\), while the peak at \(~320\text{v/cm}\) could be due to diabatic ionization of the same Rydberg state. Thus, the signal enhancement appears to be due to field ionization of high-\(n\) Rydberg atoms.

A further confirmation of this assignment is provided by the time development of the anomalous signal. By varying the time between excitation and field ionization over the range 3-12\(\mu\text{sec}\), the time dependence of the excited state population can be determined. The population of the anomalous feature was observed to decay with a characteristic lifetime of \(~30\mu\text{sec}\), which is comparable to the natural lifetime of a Rydberg state with \(n\) in the high 30s. Thus, by both SFI and lifetime considerations, the anomalous feature was identified as a Rydberg state of \(n \sim 37\).
Figure 7. SFI of the left unexpected feature in the laser scan of figure 6.
III.C. Identification as Cs**

The SFI technique provides valuable information about the quantum state distribution of Rydberg atoms; but, as only electrons are detected, it yields no information about the particular atomic species involved. In order to identify the positive ion products of SFI, TOFMS was used. The extraction voltage was chosen to exceed the field necessary to ionize the Rydberg atoms comprising the anomalous feature so that the resultant ion core could be detected. The mass spectrum obtained in this way is shown in figure 8. Surprisingly, the major peak, at mass 133, corresponds to Cs+. Secondary peaks due to Rb+, Rb2+, and RbCs+ are also visible. A spectrographic assay of the rubidium metal provided by the supplier lists cesium as the major contaminant at a level of 1 part per 1000. Although the percentage of cesium in the alkali beam will be slightly greater than in the solid, due to the higher Cs vapor pressure, the process responsible for the Cs Rydberg atom production clearly must be very efficient for a measurable signal to be observed.

In order to facilitate investigation of the anomalous feature, the alkali oven was refilled with pure cesium metal. This produced an enormous increase in the Cs Rydberg signal, indicating that the excitation process did not involve the rubidium in any way.
Figure 8. Positive ion mass spectrum taken with laser frequency set for left unexpected feature of figure 6.
III.D. Identification of the Excitation Process

Although the anomalous feature had been identified as a Cs Rydberg state, the excitation process at the observed frequency was not obvious. While the energy necessary to excite Cs(37F) from the atomic ground state is 31326\,cm$^{-1}$, two photons at the laser operating wavelength of 5943\,\AA\ give 33654\,cm$^{-1}$. Indeed, the wavelength of the exciting laser is above the two-photon ionization threshold of the ground state Cs atom, 6369\,\AA.

The second excited state of atomic Cs is the $5^2\text{D}_{3/2}$ state with energy 14499.5\,cm$^{-1}$. The energy difference between this low-lying excited state and the 37F state is 16827\,cm$^{-1}$, corresponding to a wavelength of 5943\,\AA. Based on this, it appears that the observed Cs Rydberg state is excited from the $5^2\text{D}_{3/2}$ state:

$$\text{Cs}(\,5^2\text{D}_{3/2}) \, + \, h\nu \rightarrow \text{Cs}(37\text{F}) .$$

The observation of one well-defined Rydberg state suggests that other Rydberg states may be produced by the same process at slightly different frequencies. Indeed, a search for excited states adjacent to the Cs(37F) state yielded not one, but two complete Rydberg series: the previously observed series based on Cs($5^2\text{D}_{3/2} \rightarrow n\text{F}$) transitions with a series limit at $\sim$5914\,\AA\ and a second series arising from Cs($5^2\text{D}_{5/2} \rightarrow n\text{F}$) transitions with a series limit at $\sim$5948\,\AA. In both series Rydberg atoms were produced with \textit{n} up to $\sim$150, however individual states of higher \textit{n} could not be resolved primarily due to stray electric fields in the interaction region. The observed high-\textit{n} limits of both series are shown in figure 9, which is a compilation of continuous 20\,GHz laser scans over a range of about 2\,\AA.
Figure 9. The observable high-n limits of the two Rydberg series. (a) The \(5^2D_{5/2} \rightarrow n^2F\) series near 5948 Å.
Figure 9. (b) The \(5^2D_{3/2} \rightarrow n^2F\) series near 5914 Å.
Although the excitation of high-n Rydberg atoms at the observed wavelengths had been explained, the presence of the low-lying excited atomic states remained a mystery. A possible explanation is that Cs₂ dimers are excited by a single photon to a continuum molecular state which subsequently dissociates into a 5D atom and a ground state atom. This mechanism is appealing because it allows for the production of excited states over a broad range of wavelengths as experimentally observed.

Further evidence for a dimer interaction is provided by varying the alkali oven temperature when it is loaded with rubidium metal containing the cesium impurity. An 8GHz laser scan covering the Rb(56d) states and the original anomalous feature taken with the oven operating at 235°C is shown in figure 10. Comparison with a scan over the same frequency range with oven temperature of 200°C (see figure 6) indicates that the Cs(37F) feature is greatly enhanced relative to the Rb Rydberg signal at the higher oven temperature. As noted in section 11.A.2.a), the dimer to monomer ratio rapidly increases with increasing temperature, while the Cs to Rb monomer ratio will actually decrease at the higher oven temperature. A two-photon excitation scheme in which a dissociating state of the diatomic molecule forms a resonant intermediate step is thus consistent with the observations.
Figure 10. Laser scan near 5943Å with oven temperature increased to 235°C. Note the enhancement of the Cs(37F) signal as compared to figure 6.
IV. Analysis

The excitation process discussed in the previous chapter has, in fact, been investigated by several other researchers. Collins, et. al., reported the first observation of two-photon excitation of atomic cesium through resonant continuum molecular states in 1974. They observed not only the \( (5^2\text{D} \rightarrow n^2\text{F}) \) series detected here, but also a series corresponding to \( (6^2\text{P} \rightarrow n^2\text{D}) \) transitions at shorter wavelengths. These processes have been used as sources of both low-lying excited state atoms and high-\( n \) Rydberg atoms. The following section gives an analysis of some interesting aspects of the process and highlights new insights provided by the present measurements.

IV.A. Molecular States

The first question to be answered in discussing the excitation process is the identity of the molecular states involved. Although information on the molecular states of cesium is scarce, Collins, et. al., suggest a possible energy level structure for \( \text{Cs}_2 \) (reproduced as figure 11), which represents a compilation of various other works. The ground state of \( \text{Cs}_2 \) corresponds to the \( ^1\Sigma_g^+ \) state and has a dissociation energy of \( 3630 \text{ cm}^{-1} \). Two ground state atoms can form not only the tightly bound \( ^1\Sigma_g^+ \) state, but also a repulsive \( ^3\Sigma_u^+ \) state. The triplet state, however, does have a small Van der Waals minimum located at an internuclear separation of 7-8 Å with well depth reported to range from 60 cm\(^{-1}\) to 170 cm\(^{-1}\).
Figure 11. Illustrative potential energy curves for Cs2 after Collins, et al.8
The energy level diagram illustrates that transitions to states that dissociate into a 5D atom could occur for present photon energies from two possible initial populations: vibrationally excited weakly bound $^1\Sigma_g^+ (v \to \infty)$ states; or the Van der Waals bound population of the $^3\Sigma_u^+$ state. Transitions from these initial states differ not only in energy, but also in the internuclear separation at which absorption would likely occur. The following table summarizes the threshold wavelength for production of dissociating states with a single photon and the characteristic internuclear separation for both of the two populations noted above.

<table>
<thead>
<tr>
<th>State</th>
<th>Long wavelength limit for 5D atom</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma_g^+ (v \to \infty)$</td>
<td>~6850 Å</td>
<td>4-8 Å</td>
</tr>
<tr>
<td>$^3\Sigma_u^+$</td>
<td>~6850</td>
<td>7-8</td>
</tr>
</tbody>
</table>

Note that transitions to dissociating states from the strongly bound $^1\Sigma_g^+(v=0)$ state are energetically forbidden for photon wavelengths longer than \~5500Å. In order to further identify the production mechanism, the energetics of the process must be better understood.

An indication of the molecular states involved is provided by observing the dissociation energy imparted to the atomic products since this reflects the energy above the separated atom limit at which excitation
occurs. This energy, which appears as kinetic energy of the 6S and 5D atoms as they separate, can be determined from measurements of the velocity of the atoms by observing the Doppler profiles of the Rydberg states which are excited from the dissociated 5D atoms. As noted previously, the linewidth of the dye laser is $\sim 250$kHz and the observed peak width of Rydberg states produced by normal transverse excitation of ground state atoms is $\lesssim 80$MHz. Therefore, the 16Hz width of the Cs Rydberg atom peaks, as observed in both this work and previous investigations, represents the Doppler broadened width of the 5D$\rightarrow$nF transition.

By numerically fitting the observed Rydberg peak profiles to a Gaussian lineshape, the average kinetic energy of the 5D atoms after dissociation was determined. Sample peak profiles and the corresponding Gaussian fits for the two Rydberg series are shown in figure 12. The dissociation energy, $\Delta E$, is simply twice the kinetic energy of the 5D atom as the two Cs atoms, being of equal mass, carry off equal amounts of energy. The $\Delta E$s differ for the two observed series, with calculated values of

\[
\Delta E (5^2D_{5/2} \rightarrow nF) = 1100 \pm 100 \text{ cm}^{-1}
\]

\[
\Delta E (5^2D_{3/2} \rightarrow nF) = 1550 \pm 150 \text{ cm}^{-1}
\]

These dissociation energies represent approximately 65meV and 95meV per particle, which is roughly twice thermal energy. Furthermore, as the intermediate state is most likely excited at an energy of $\Delta E$ above the energy of the separated atom limit, the total excitation energies are

\[
E (5^2D_{5/2} - 6^2S_{1/2}) = 15700 \text{ cm}^{-1}
\]

\[
E (5^2D_{3/2} - 6^2S_{1/2}) = 16050 \text{ cm}^{-1}
\]
Figure 12. Observed doppler profiles and fits to Gaussian lineshapes. (a) $5^2D_{3/2} \rightarrow 85^2F$ and 95meV fit.
Figure 12. (b) $^{52}D_{5/2} \rightarrow 85^2F$ and 65meV fit.
Since the energy of the exciting photons is \( \sim 16800 \text{cm}^{-1} \), we are led to conclude that photoexcitation must occur from an initial molecular state lying \( \sim 800-1000 \text{cm}^{-1} \) below the ground state separated atom limit. Thus excitation must occur primarily from the molecules in highly vibrationally excited \( \tilde{X}^1\Sigma_g^+ \) states. Transitions from the Van der Waals bound \( ^3\Sigma_u^+ \) state would leave the product atoms with \( \sim 1000 \text{cm}^{-1} \) more kinetic energy than observed, corresponding to a factor of 2 increase in the Doppler width.

Thus, the initial molecular state population responsible for the production of the 5D atoms has been identified; however, the intermediate dissociating state has yet to be determined. While the intermediate state may be repulsive in character, it is more likely that the continuum of the bound \( \text{Cdm}(^1\Pi_u) \) state, previously suggested to dissociate to a 5D atom\(^{15} \), serves as the dissociating state. The minimum of the \( ^1\Pi_u \) potential curve lies at approximately the same internuclear separation as the minimum of the \( \tilde{X}^1\Sigma_g^+ \) state. Therefore, transitions would likely occur for the smallest \( R \)'s energetically allowed, as this provides the maximum wavefunction overlap between initial and final molecular states in accordance with the Franck-Condon principle.

The excitation sequence, as illustrated in figure 13, begins with absorption from near the top of the potential well of the \( \tilde{X}^1\Sigma_g^+ \) bound state to the continuum of the \( \text{Cdm}(^1\Pi_u) \) state,

\[
\text{Cs}_2(^1\Sigma_g^+) + h\nu \rightarrow \text{Cs}_2(\text{Cdm}^1\Pi_u),
\]

followed by dissociation of the intermediate state,

\[
\text{Cs}_2(\text{Cdm}^1\Pi_u) \rightarrow \text{Cs}(5^2\text{D}) + \text{Cs}(6^2\text{S}),
\]
and finally absorption of a second photon to a Rydberg state,

\[ \text{Cs}(5^2D) + h\nu \rightarrow \text{Cs}(n^2F). \]

Figure 13. Mechanism for 5D atom production. A molecule in a highly-vibrationally excited \(^1\Sigma_g^+\) state is photoexcited to the continuum of the \(^1\Pi_u\) state. \(\Delta E\) is the dissociation energy.
It should be noted that Collins, et. al.,\textsuperscript{9} favor excitation from the $^{3} \Sigma_u^+$ state to an intermediate repulsive $\text{d} \pi (^{3} \Pi_g)$ state as the 5D atom production mechanism. However, the linewidth of their dye laser, $\approx \text{6GHz}$, exceeded the Doppler width of the 5D→nF transition precluding observation of the dissociation energy of the product atoms. Lacking this information, their preference of the $^{3} \Sigma_u^+$ state as the initial state is based solely on a prejudice for large $R$ transitions over those at smaller $R$ to excite dissociative states.

\textbf{IV.B. Feasibility}

Although the proposed excitation process is energetically valid, it remains to demonstrate that the process can be solely responsible for the very large Rydberg atom signals observed. In order to determine the feasibility of the scheme, two further considerations must be addressed: the available population of highly vibrationally excited $^1 \Sigma_g^+$ molecules and the lifetime against dissociation as compared to the excited state lifetime.

The existence of molecular states in the wavelength region of interest is demonstrated by the experimentally observed $0.2 \AA^2$ photoabsorption cross-section in the range 5700–6000\AA\ for Cs$_2$\textsuperscript{20}. This significant absorption qualitatively suggests the availability of continuum states of suitable energy for the intermediate step of the photoexcitation process.

In addition, the number of molecules with the proper initial energy can be quantitatively estimated. The concentration of diatomic molecules in the alkali beam, as discussed previously (see section \textbf{II.A.2.a}), is
\( \sim 2 \times 10^6 \) cm\(^{-3} \) at the center of the interaction region. The dimers will be confined to the ground electronic state, but will have a thermal Boltzmann distribution of vibrational and rotational energy with characteristic temperature given by the exit aperture of the alkali oven, \( \sim 490^\circ \)K. The relevant molecular constants for \( \text{Cs}_2 \) are\(^{21} \)

\[
\begin{align*}
\omega_e &= 42.022 \text{ cm}^{-1} \\
\omega_e x_e &= 0.0823 \text{ cm}^{-1} \\
B_e &= 0.0127 \text{ cm}^{-1}.
\end{align*}
\]

Due to the \((2J+1)\)-fold degeneracy of a state with rotational angular momentum \( J \), the distribution of rotational states is not given simply by the Boltzmann factor. Instead, the number of molecules with a given \( J \) is proportional to

\[
(2J+1) \times \exp[-B_e J(J+1) \hbar^2 c/k T] .
\]

This function increases as \( J \) increases until a maximum, given by

\[
J_{\text{max}} = [k T/(2B_e \hbar c)]^{1/2} - 1/2
\]

is reached and then decreases as the angular momentum further increases. For the present case, \( J_{\text{max}} = 115 \) and there is clearly a wide spread of closely-spaced rotationally excited states.

In contrast to the rotational case, the vibrational state distribution is governed simply by the Boltzmann factor. The vibrationally excited population is a strictly decreasing exponential function of the vibrational energy. In order for transitions to dissociating intermediate states to occur, the initial state must lie 5-10 kT (2000-3600 cm\(^{-1} \)) above the ground vibrational state of the \( X^1\Sigma_g^+ \) band. The fraction of molecules in this energy range is only \( \sim 2\% \) of the total number of dimers, leading to a density of
suitable initial molecules of $4 \times 10^4 \text{cm}^{-3}$ in the interaction region. The total number of available molecules illuminated per second is given by the flux through the laser beam:

$$N = A \rho \nu$$

where $A$ is the cross-sectional area of the intersection of laser and alkali beams, $\rho$ is the vibrationally-excited dimer density, and $\nu$ is the mean velocity of the dimers. Substituting for the values of these parameters yields

$$N = 2 \times 10^6 \text{ per second} .$$

With the high power density of the focused dye laser beam, near saturation of the transition to intermediate dissociating molecular states is expected. Furthermore, photoexcitation rates for the atomic (5D$\rightarrow$nF) transition should be $\geq 10^5 \text{ sec}^{-1}$ for atoms whose transition frequencies lie within $\sim 100 \text{kHz}$ of line center$^{22}$. Calculations indicate that roughly 0.3% of the 5D atoms should be excited to high-$n$ Rydberg levels for the present conditions, therefore the observed count rates of $\sim 10^4$ Rydberg atoms per second are not unreasonable.

In order for the second step of the process to be achieved, the Cs atoms must separate in a time less than both the excited molecular state lifetime and the residence time of the excited atoms in the laser beam. Based on the observed dissociation energies, the lifetime of the intermediate state molecule against dissociation should be only a few picoseconds. This is indeed much shorter than the radiative lifetime of the 5D atom, calculated$^{23}$ and experimentally observed$^{24}$ to be on the order of 1$\mu$sec, indicating that the 5D atom escapes while still excited. At the observed dissociation energies, the separated atoms will remain in the
laser beam for ~10nsec allowing time for absorption of a second photon leading to excitation of the Rydberg atoms.

IV.B. Miscellaneous Observations

Two other aspects of the process are worthy of note here: the photoexcitation of higher angular momentum Rydberg atoms through Stark induced mixing with the adjacent F states and the observation of a Rydberg series of nP atoms excited by (5D→nP) transitions. Both features were identified through a knowledge of the quantum defects of the states involved, which for cesium in the high-\(n\) range are\(^{24}\)

\[ \delta_p \approx 3.58 \]
\[ \delta_F \approx 0.0336 \]

The very small quantum defects of the \(nF\) states of Cs indicate that they are very nearly hydrogenic in character. However, there is a small energy separation between the F states and the higher angular momentum states at a given \(n\), suggesting that a relatively weak electric field can mix the energy levels of the high \(l\) manifold with the F state energy level. In this case, \(l\) is no longer a good quantum number and transitions to high angular momentum states that are optically forbidden in zero electric field can occur. Thus, by applying a DC electric field of as little as a few volts per cm across the interaction region, it should be possible to photoexcite states of the high \(l\) manifold which have sufficient F-like character. This was indeed observed (see figure 14). The feature to the left in the laser scan of figure 14 is due to 37F Rydberg atoms, while the right feature corresponds to the \(n=37\) manifold. Calculated energy levels predict a zero-field energy separation of 4.4GHz, in good agreement with the observed profiles.
Figure 14. Laser scans taken with varying DC electric fields in the interaction region showing excitation of the Cs(37) high I manifold.
(a) 0.0v/cm; (b) 0.5v/cm; (c) 1.1v/cm.
Comparison of the above quantum defects indicates that the nP state should lie halfway between the (n-4)F and (n-3)F states in energy. This was indeed observed as illustrated in figure 15. The small, double-peaked feature midway between the 80F and 81F states corresponds to Cs(84P) atoms. The fine structure interval between $84P_{1/2}$ and $84P_{3/2}$ is only 0.1GHz, which is insufficient to account for the 1GHz separation of the dual peaks. Therefore, the double-peaked nature is most probably due to Stark splitting of the fine structure levels by a small stray electric field in the interaction region. The series of (5D→nP) transitions has not been reported in the literature, as the weak signal it produces is dominated by the strong signal due to the fundamental series. However, the small linewidth of the exciting dye laser, low background noise level, and sensitivity to single excited atoms permitted observation of the nP series in the present work.
Figure 15. (a) Laser scan showing photoexcitation of Cs(88P) states as part of the \(5^2D_{3/2} \rightarrow nP\) Rydberg series. (b) 10x magnification.
V. Conclusion

The photoexcitation of cesium to Rydberg states through resonant dissociative states of the dimer has been investigated. Although the investigation had a rather humble beginning with the observation of two small unexpected bumps in a laser scan, it proceeded to an independent identification of the process and provided new insights into the phenomenon. In addition, the process is of interest beyond mere curiousity.

One useful application of the process is in the study of molecular state potential energy curves. Information about the shapes of both the initial and final states can be gained by varying the excitation energy. Perhaps the most versatile experimental set-up for investigating the molecular states would be a two laser system with one laser at fixed frequency to excite an atomic high-n Rydberg transition thus providing detection of the dissociation products. The frequency of the second laser could then be varied in order to probe the energy dependence of the molecular transition. This technique would thus be sensitive over photon energy ranges at which the two steps of the photoexcitation process are not simultaneously resonant.

A second application of the process is the production of excited atoms. This investigation has demonstrated the feasibility of the process as a state-selective Rydberg atom excitation source. Copious quantities of Rydberg atoms with $n$ up to 150 have been produced by the photoexcitation of Cs through dissociative states of Cs$_2$. Furthermore, very nearly hydrogenic $n$F states can be prepared in this manner. These aspects are potentially beneficial to the ongoing Rydberg atom research conducted in this laboratory. Rydberg atoms excited in this way could be used to extend present collision studies to very low electron energies. One study of
particular interest is to investigate the n-dependence of electron attachment interactions between very high-n Rydberg atoms and target molecules such as SF$_6$ and C$_7$F$_{14}$. 
V. References


22. See, for example, A. Yariv, Quantum Electronics, John Wiley and Sons, New York, 1967.
