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STUDIES OF AUTOIONIZING STATES RELEVANT TO DIELECTRONIC
RECOMBINATION

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ABSTRACT

An important loss process in CTR plasmas is the process of dielectronic recombination, which proceeds via autoionizing states. At this date, however, this problem is not fully understood, largely because of the nearly complete lack of fundamental atomic data on highly excited autoionizing states. In this document, we outline the continuation of a program to investigate the properties of autoionizing states of alkaline earth metals by means of a novel laser excitation technique developed at SRI. This approach will allow us to study, for the first time, autoionizing states of arbitrary n , and ℓ in a controlled environment. Specifically, we plan to measure autoionization rates and branching ratios as a function of n and ℓ and the effects of electric fields. These experiments should yield the basic atomic data, autoionization rates, required as inputs to sophisticated model calculations of dielectronic recombination rates.

I INTRODUCTION

Configuration interaction occurs in many contexts in atomic physics with widely varying results. For example, in the bound series converging to the first ionization limit there frequently exists a state which is a low lying member of a series converging to a higher ionization limit. Such a state, which is frequently called a perturber, is usually coupled via configuration interaction to the series converging to the first limit with the result that the energies of nearby members of the bound series are displaced. This effect only occurs for atoms in which the higher ionization limits are not far separated from the first, excluding, for example, He and the alkali atoms. The more general, and perhaps more interesting, manifestation of configuration interaction occurs above the first ionization limit, for here all states converging to higher limits experience configuration interaction with the continuum and hence autoionization. While configuration interaction is clearly within the realm of spectroscopy, the ejection of an electron coupled with the deexcitation of the remaining ionic core is the inverse of a collision process--electron capture. Consequently, autoionization occupies a rather unique position between two branches of atomic physics usually viewed as quite separate.

In addition to its intrinsic interest, autoionization has considerable practical importance, ranging from the development of new xuv lasers¹ to the analysis of the temperature of solar plasmas.² Perhaps the most important practical role is played by the inverse of autoionization, dielectronic recombination, which lowers the ionization balance in CTR plasmas, thereby producing an important source of radiative power loss.³

This document describes the research plan for the third year of Contract No. DE-AT03-ER10376, under which we have been studying the basic atomic physics of autoionizing states relevant to dielectronic recombination using a novel and powerful laser excitation technique developed at SRI.⁴

In the following sections, we briefly outline the important features of dielectronic recombination, the progress to date this year, and the proposed experimental program. This is followed by a summary of our qualifications and the statement of work.

II DIELECTRONIC RECOMBINATION IN He-LIKE SYSTEMS

Dielectronic Recombination and Autoionization

In the tokamak plasmas the dominant dielectronic recombination processes occur in not quite fully stripped ions, namely, He-like or Li-like systems. Although the recombination processes of both He-like and Li-like systems are important, we focus on He-like systems, mainly because we now have the capability to study He-like systems experimentally in great detail. We consider He-like systems to be any system with two valence electrons outside a closed shell core. Typical examples are HeI, LiII, FeXXIV (a typical tokamak impurity ion), and alkaline earth atoms MgI, CaI, SrI, and BaI. The systematic study of these atoms should provide the essential data base for understanding the basic features of all He-like systems.

We would like to stress that the autoionizing Rydberg states of the alkaline earth atoms, in which one of the two valence electrons is far from the ionic core, are physically similar to highly stripped atomic species. This is because the essential properties of the alkaline earth autoionizing states are determined by the interaction of the two valence electrons, and the electrons in the closed shells play no real role. Thus, the only substantial difference between the autoionizing Rydberg states of alkaline earth atoms and highly stripped He-like species is the charge state of the ionic core, which may be easily accounted for theoretically. Consequently, we have centered our attention on the alkaline earth atoms, which may be studied in detail using tunable dye lasers and therefore offer the greatest physical insights for a relatively modest effort.

Dielectronic recombination may be viewed as a two-step process: electron capture followed by radiative decay, processes (1) and (2).²

In this discussion we assume that autoionization only occurs to the ground state of the ion. Since we plan to do experiments with Sr in the coming year, let us use Sr as a concrete example for a description of the process.

Figure 1 shows the relevant energy levels of Sr and Sr^+ . In the electron capture process, indicated by Eq. (1), an electron colliding with a Sr^+ ion excites the valence electron of the ion from its ground state 5s into an excited state, say 5p, and is captured itself, leaving the atom in an autoionizing state $5pn\ell$. Here we follow the convention of labeling the state of the atom by the states of the two electrons. (As mentioned above, we consider only the two valence electrons.) That is, $\text{Sr } 5pn\ell$ is a Sr atom with one electron in the 5p state and the other in the $n\ell$ state. Usually we will call the first electron, the 5p electron in this case, the "inner" electron, and the second, the $n\ell$ electron, the "outer" electron because in the planned experiments $n \sim 10$. In general, the final state of the captured electron as well as that of the inner electron may be an arbitrary state---for example, $\text{Sr } n'\ell'n\ell$.

As mentioned above, the second step of dielectronic recombination is radiative decay, indicated by Eq. (2). In our example of Sr, the autoionizing $5pn\ell$ state radiates to the $5sn\ell$ state, which is bound. As shown by Figure 1, the wavelength of this radiation is similar to the 5p-5s radiation of the Sr^+ ion. Typically, the presence of the spectator electron shifts the wavelength of the emitted radiation from the wavelength of the ion line. In fact, the observation of satellite lines shifted from ion lines in both laboratory and astrophysical plasmas^{2,5} prompted the suggestion of the mechanism of dielectronic recombination by Burgess.⁶ Since the $\text{Sr } 5pn\ell$ state is an autoionizing state, it may autoionize, and this process, indicated by Eq. (3), competes with radiative decay. If the atom autoionizes, the net result of the whole process is nil; that is, no recombination occurs. Thus, the competition between radiation and autoionization plays an important role in the determination of the dielectronic recombination rate.

We can express the dielectronic recombination rate, A_{DR} , for any state as the product of the electron capture rate and the fluorescence yield, w . Explicitly

$$A_{\text{DR}} = A_{\text{EC}} \cdot w \quad (4)$$

Here A_{EC} is the electron capture rate and w is the fluorescence yield for the state under consideration. Since electron capture, Eq. (1), is exactly the

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FIGURE 1 RELEVANT LEVELS OF Sr AND Sr^+

inverse of autoionization, Eq. (3), for any autoionizing state, the electron capture rate is proportional to the autoionizing rate.³ Taking advantage of this fact and writing the branching ratio explicitly, we can write the dielectronic recombination rate as

$$A_{DR} \propto \frac{A_A \cdot A_R}{A_A + A_R} \quad (5)$$

where A_A and A_R are the autoionization and radiative decay rates, respectively. From Eq. (5), it is apparent that those states with autoionization rates much greater than the radiative decay rates have dielectronic recombination rates that scale as A_R . For the states with much faster radiative than autoionization rates, the dielectronic recombination rate scales as A_A .

Autoionization and Radiative Decay Rates

In our example of Sr, the $5pn\ell$ states all have radiative decay rates of $\sim 10^8 \text{ s}^{-1}$, regardless of n and ℓ , because the predominant radiative decay of the Sr $5pn\ell$ state is to the $5sn\ell$ state. The transition involves only the "inner" electron transition $5p \rightarrow 5s$. Essentially, this is the $5p-5s$ resonance transition of the Sr^+ ion with a spectator electron in the n, ℓ orbit. Consequently, the radiative decay rate is that of the Sr^+ $5p$ state, 10^8 s^{-1} . Autoionization rates have been shown to scale as $(n^*)^{-3}$, as might be expected from core penetration arguments. Here n^* is the effective quantum number of the outer electron. That is, the binding energy of the outer electron is $\frac{1}{2}(n^*)^{-2}$. Frequently, n^* is expressed as $n - \delta$, where δ is the quantum defect. For the lowest ℓ states of the alkaline earth atoms $\delta \sim 2$, and for the highest ℓ states $\delta \sim 0$. The ℓ dependence of the autoionization rate is not clear as yet, although our preliminary measurements indicate a rapid decrease in the autoionization rate with ℓ ,⁴ and our calculations for high ℓ states indicate that for high ℓ the autoionization rates should scale as ℓ^{-4} .⁷ This is in good agreement with the measurements of autoionization rates we have made under this contract, although the measurements are not a stringent test of the theory. Because of the high statistical weight of the high ℓ states, accurate determination of their autoionization rates is important.

Thus far, we have considered only those changes in the autoionization

rate that depend on the state of the outer electron. As we excite the inner electron to higher states, a simple He-like picture suggests that the overlap of the radial wave functions of the two electrons will decrease and that, therefore, the autoionization rate will also decrease. However, the radiative decay rates are also decreased by further excitation of the inner electron, scaling approximately as n^{-3} . For example, the Sr $6sn\ell$ and $6pn\ell$ states have longer radiative lifetimes than the $5pn\ell$ states. Again, we expect that these lifetimes will be very close to the lifetimes of the $Sr^+ 6s$ and $6p$ states. Although the dependence of the Sr $6pn\ell$ autoionization rates on n and ℓ of the outer electron would be similar to that of the $5pn\ell$ states, the overall dielectronic rate would be lower because of the slower radiative decay rate of the $6pn\ell$ states.

Since autoionization plays such a central role in dielectronic recombination, it is apparent that extensive data on autoionization rates are necessary to reach a quantitative understanding of dielectronic recombination. At present, virtually all the information available is limited to autoionizing states that are optically accessible from the ground or low-lying states of the atom via configuration mixing.⁸ By virtue of the dipole selection rules, such studies have been limited to autoionizing states of angular momentum. Until our preliminary measurements,⁴ no data were available on any aspect of the higher ℓ states.

Perturbations by Electric Fields

A plasma contains a high density of ions and electrons that, while macroscopically neutral, produce substantial microscopic electric fields. Jacobs et al.⁹ have studied this problem theoretically, and their results show that the presence of the microscopic fields leads to increased autoionization rates. Basically, this occurs because the electric fields destroy the spherical symmetry of the atoms, with the result that ℓ is no longer a good quantum number. Thus, in a field, the familiar angular momentum states are no longer the good quantum states; rather, the parabolic Stark states, which we shall denote with the quantum number k , are the good quantum states. From the point of view of dielectronic recombination, the most important effect of this is that the autoionization rates are not the same as they are in the zero field ℓ states. In general, the autoionization rates of the Stark states

will tend toward the average rate of all the ℓ states of the n manifold since the Stark states are linear combinations of the ℓ states. This "averaging" should dramatically increase the autoionization rates of the high ℓ states, thereby increasing the net dielectronic recombination rates because of the higher statistical weights of the higher ℓ states.⁹ Under this contract, we have begun the systematic study of autoionization of Ba in electric fields, and our results to date support the theory of Jacobs et al.⁹

Collisional Effects

In addition to producing electric fields, the ions and electrons of the plasma collide with the atoms in the autoionizing states, and the effects of such collision processes have been studied theoretically.⁹⁻¹¹ One important process that occurs is collisional angular momentum mixing (ℓ mixing) of the autoionizing states by ion and electron collisions.^{7,9} This process is particularly important because of the large cross sections for ℓ mixing by ions and electrons. Electrons at temperatures $\sim 10^6$ K (100 eV) have been shown to have cross sections $> 10^{-10}$ cm² for angular momentum mixing for bound states,¹² and the cross sections for angular momentum mixing by ion collisions are calculated to be at least an order of magnitude larger.⁹ This can significantly redistribute populations from the low ℓ autoionizing states, which have high electron capture cross sections (and autoionization rates), to the high ℓ states, which have autoionization rates lower than the radiative decay rates. This produces a greatly enhanced dielectronic recombination rate.

As an example of what could happen, let us consider the $n = 10$ manifold of Sr. Our measurements indicate that the Sr 5p10d state has the highest autoionization rate and therefore has the highest electron capture cross section in a collision with an electron. Thus, Sr⁺ is most likely to capture the electron into the 5p10d state, of all the 5p10 ℓ states. In the absence of collisions, only a small fraction of the Sr 5p10d atoms decay radiatively; most autoionize. However, electron and ion collisions can redistribute the electrons originally captured into the Sr 5p10d state into the higher ℓ states, such as 5p10h, which have slower autoionization rates and are thus more likely to decay radiatively. Therefore, collisions can combine the high electron capture cross sections of the lower ℓ states with the high

fluorescence yields of the higher λ states to produce a much higher net dielectronic recombination rate.

III PROGRESS DURING THE CURRENT YEAR

During the current year we have worked on several projects, mainly, this study of "forced autoionization,"¹³ the development of an electron energy analysis capability, and a more systematic analysis and presentation of our earlier data on the Ba 7snd states. In this section we present detailed reports of each of these tasks.

Forced Autoionization

The basic concept of forced autoionization is best explained using the case we have studied in detail. In Ba, the $5d7d^1D_2$ valence state perturber lies just below ($\sim 200 \text{ cm}^{-1}$) the first ionization limit ($\text{Ba } ^+6s$). It is a state with both electrons excited (5d, 7d), but to small orbits of $\sim 10 \text{ \AA}$ in diameter. Since it is so close to the first ionization limit, it falls in the 6snd Rydberg series between $n = 26$ and $n = 27$. The 6snd Rydberg states have similar energies but have completely different properties. One electron is in the 6s ground state and the other is in a large Rydberg orbital of $\sim 600 \text{ \AA}$ diameter. Since the parity and total angular momenta of the perturber and the Rydberg series are the same, they interact, and in zero field this is manifested in a displacement of the term energies and quantum defects of 6snd states in the vicinity of the 5d7d perturber, as shown in Figure 2, a Lu-Fano plot of the quantum defects.¹⁴ From quantum defect analysis of the state energies it is, in fact, possible to determine the strength of the configuration interaction between the 5d7d perturber and the 6snd Rydberg series.¹⁵

Forced autoionization is essentially a direct method of probing the strength of the configuration interaction. To a first approximation, when we apply a field $\sim 2000 \text{ V/cm}$, the 6snd states are converted to a quasi-continuum and the discrete 5d7d state becomes a resonance. Thus, if we photoexcite states in this vicinity, we expect to see interference between the quasi-continuum due to the 6snd states and the 5d7d state leading to an asymmetric Beutler-Fano profile,¹⁶ the width of which gives directly the strength of the configuration interaction.

It is worth noting that the phenomenon of forced autoionization was first observed (and given this name) by Garton et al.¹³ in shock tube experiments. However, they were not able to quantitatively study the effect. When we began

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FIGURE 2 LU-FANO PLOT OF THE Ba 6 AND STATES
 $6 \text{ snd } ^3D_2$ ($\square$), $6 \text{ snd } ^1D_2$ ($\circ$), $5d7d \ ^1D_2$ ($\triangle$)

this work as a quantitative, systematic study of forced autoionization, our understanding was approximately as stated above. Since then another study has been reported which indicated that the above picture is completely adequate.¹⁷ However, from our work it is quite apparent that the process was considerably more subtle, as we shall describe.

The approach we employed was two-step laser excitation of states in the vicinity of the $5d7d^1D_2$ state using two intermediate states as shown in Figure 3. Using path A of Figure 3, excitation to the 6snd Rydberg series or quasi-continuum is stronger, and, using path B, excitation to the $5d7d$ perturber is stronger. The experiment consisted of taking excitation spectra by sweeping the wavelength of the second laser in either case.

There are two basic results from this experiment. First, the strength of the configuration mixing with and without the field is about the same. This can be seen from the spectra taken via path A of Figure 3. In Figure 4 we show the zero field excitation spectrum and the spectrum taken at $E = 4.8$ kV/cm. Note that there is a minimum in the signal in both traces at ~ 41481 cm^{-1} , but that it is only in the $E = 4.8$ kV/cm case that we are easily able to discern the characteristic Beutler-Fano profile and measure its width, which we determined to be 15.5 cm^{-1} in contrast to 20 cm^{-1} from the quantum defect analysis. Thus, we see that the configuration interaction is not quite the same in the field. The differences are quite interesting and become more apparent as we take a closer look.

The second important result is revealed by detailed examination of the spectra taken using path B. In Figure 5 we show the spectra of the $|m| = 1$ states in a field of 7.5 kV/cm. Note that it is apparently a smooth Beutler-Fano profile, which gives a configuration interaction of 15.5 cm^{-1} . However, the $|m| = 0$ spectrum has sharp spikes that interfere positively on one side of the main $5d7d$ profile and negatively on the other as shown by Figure 6. The sharp spikes originate from the long lived $|m| = 0$ Stark states,¹⁸ which together with the smooth 6snd $|m| = 0$ quasi-continuum form a highly structured continuum with which the $5d7d$ state interacts. To our knowledge this is the first observation of the interaction of a state with a well-defined structured continuum. In addition, these observations show clearly that the electric field has destroyed the Coulomb nature of the wavefunctions of the atom and, hence, quantum defect theory is not applicable. This is essentially the

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FIGURE 3 EXCITATION SCHEME SHOWING PATHS
A AND B

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FIGURE 4 EXCITATION SPECTRA USING PATH A IN FIELDS OF 0 AND 4.80 kV/cm

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FIGURE 5 $|m| = 1$ EXCITATION SPECTRUM USING PATH B AND THE COMPARISON TO ZERO FIELD MQDT RESULTS

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FIGURE 6 $m = 0$ EXCITATION SPECTRUM USING PATH B

opposite of the conclusion of Cole et al.¹⁷

To reach a quantitative understanding of the observed spectra, we have used the configuration interaction theory of Fano to fit the data assuming that the 5d7d state is interacting with a structured continuum, and to our knowledge this is the first example of the application of the theory to a problem involving strongly energy-dependent interaction matrix elements. In fitting our data to the theory we needed to make only a few approximations. We found that the interaction strength, 15.5 cm^{-1} of the 5d7d state with the $|m| = 1$ continuum was the same as the interaction of the 5d7d state with the smooth part of the $|m| = 0$ continuum. To represent the long-lived Stark states, we used the Ansatz of Luc-Koenig and Bachelier.¹⁹ The positions and widths of the Stark states were determined from our measurements and their known field dependence. The interaction strength between the long lived Stark components and the 5d7d state was left as the only free parameter, after assuming that all the Stark components have the same interaction strength to minimize the number of free parameters.

The results of fitting our data are typified by the example shown in Figure 7, which is a plot of the measured and fit differences between the structural curves (as in Figure 6) and a smooth Beutler-Fano profile (as in Figure 5). As Figure 7 shows, the fit is quite good, and we are easily able to extract the interaction strength between the 5d7d states and the long-living Stark components.

We found an interaction strength of about 30 cm^{-1} for the long-lived Stark states, a value almost twice as high as for the smooth continuum. This is not too surprising since these states are localized near the center of the atom, unlike the smooth quasi-continuum, and should interact more strongly with the small 5d7d state.

In sum, this work makes it apparent that the configuration interaction with and without the electric field is qualitatively the same, but that there are important differences. In particular, the differences show the breakdown of the spherical symmetry of the atom; this implies the breakdown of quantum defect theory, which is frequently quite successfully used to treat configuration interaction at zero fields.

FIGURE 7 $|m| = 0$ DIFFERENCE SIGNALS (—) AND FITS (---) AT THREE FIELDS

Electron Energy Analysis

During this period we have been actively engaged in the construction of an electron energy analyzer to analyze the energies of the electrons resulting from autoionization. It is a 120° electrostatic analyzer with molybdenum-coated surfaces to reduce stray electric fields. It will be mounted below the interaction region as shown in Figure 8, allowing us to have the particle multiplier ion detector at the same time. The analyzer itself is completely constructed, and the mounting hardware and magnetic shield are being fabricated. We expect that it will be operational by February 1981.

Analysis of the Ba 7s_{nd} Spectra

We have made a more complete analysis of our excitation spectra, obtained last year, of the Ba 7s_{nd} states.²⁰ Previously, we had only presented data for the Ba $6p_{3/2}^{nd} \rightarrow 7s_{1/2}^{nd}$ transition. The updated analysis is included as Appendix A. Note that the title has been changed from "The Observation of Ba Planetary Atoms" to the more descriptive title "The Observation of the Ba 7s_{nd} States."

FIGURE 8 SCHEMATIC OF THE APPARATUS USED IN THE PRELIMINARY EXPERIMENTS