**Final Report of work under Grant DE-FG02-96ER14647**

**Recipient:** Colorado State University

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**Principal Investigator:** Stephen R. Lundeen

This project originated with the desire to apply the dense CW Rb Rydberg target, developed by the PI under previous NSF support, to the study of collisions between highly-charged ions (HCI) and Rydberg atoms. The feasibility of such studies was demonstrated in initial unfunded studies carried out during the summer of 1994 at Kansas State University and represented in publication [0] listed below.

[0] "Absolute cross sections for charge capture from Rydberg targets by slow highly charged ions" B.D. DePaola, M.T. Huang, S. Winecki, M.P. Stockli, Y. Kanai, S.R. Lundeen, C.W. Fehrenbach, and S.A. Arko, Phys. Rev. A52, 2136 (1995)

Supported by this initial result, funding was obtained in Sept. 1996 for a project titled:

**" Ion/Excited-Atom Collision Studies with a Rydberg Target and a $CO_2$ Laser"**.

The goal of this project was to obtain detailed studies of the charge capture collisions between both singly and multiply-charged positive ions and excited levels of Rb that form the dense Rydberg target.This work continued over the next nine years and succeeded in producing by far the most extensive and detailed experimental study of this important class of ion atom collisions. The progress is represented in publications 1-11 listed below.

[1] "Experimental studies of highly-charged ion collisions with Rydberg atoms", S.R. Lundeen and C.W. Fehrenbach, Proceedings of the 14th International Conference on the Application of Accelerators in Research and Industry, Nov. 5-9, 1996, Denton TX

[2] Absolute charge capture cross sections from a Rydberg target: Experimental results and comparison with theoretical models, M.-T. Huang, M.P. Stockli, C.W. Fehrenbach, S.R. Lundeen, and B.D. DePaola, J. Phys. B 30, 2425 (1997)

[3] "Final state distributions in resonant charge transfer ion-Rydberg collisions.", D .S. Fisher, C.W. Fehrenbach, S.R. Lundeen, E.A. Hessels, and B.D. DePaola,, Phys. Rev. A 56, 4656 (1997)

[4] "Energy transfer in charge exchange collisions between slow ions and Rydberg atoms", D.S. Fisher, C.W. Fehrenbach, S.R. Lundeen, E.A. Hessels, and B.D. DePaola , Phys. Rev. Lett., 81, 1817 (1998)

[5] "Experimental Studies of Resonant Charge Transfer from Rydberg states by Highly-Charged Ions", S.R. Lundeen, D.S. Fisher, C.W. Fehrenbach, and B.D. DePaola , Physica Scripta, T92, 71-75 (2001)

[6] "Energy transfer in Ion-Rydberg Atom Charge Exchange", D.S. Fisher, S.R. Lundeen, C.W. Fehrenbach, and B.D. DePaola, Phys. Rev. A, 63, 052712 (2001)

[7] "Experimental study of L-distributions resulting from charge capture by $Si^{3+}$, from Rydberg atoms", R.A. Komara, S.R. Lundeen, C.W. Fehrenbach, and B.D. DePaola , Phys. Rev. A 64, 052714 (2001)

[8] "State Selective charge transfer cross sections for Na+ with multiply excited rubidium: A unique diagnostic of MOT dynamics",", X. Flechard, H. Nguyen, R. Bredy, S.R. Lundeen, M. Stauffer, H.A. Camp, C.W. Fehrenbach, and B.D. DePaola, Phys. Rev. Letters 91, 243005 (2003)

[9] "Stark-induced X-ray emission from high Rydberg states of H-like and He-like Si", M.A. Gearba, R.A. Komara, S.R. Lundeen, W.G. Sturrus, C.W. Fehrenbach, B.D. DePaola, and X. Flechard, Phys. Rev. A 66, 032705 (2002)

[10] "Stark-induced X-ray emission from H-like and He-like Rydberg ions", M.A. Gearba, R.A. Komara, S.R. Lundeen, C.W. Fehrenbach, and B.D. DePaola, Phys. Rev A 71, 013424 (2005)

[11] "Relative charge transfer cross section from Rb(4d)", M.H. Shah, H.A. Camp, M.L. Trachy, X. Flechard, M.A. Gearba, H. Nguyen, R. Bredy, S.R. Lundeen, and B.D. DePaola, Phys. Rev. A 72, 024701 (2005)

The high level of detail achieved in these studies was primarily due to the use of a Doppler-tuned $CO_2$ laser to selectively detect the charge capture products in these collisions. This is most clearly demonstrated in the definitive study of the binding energies of the collision products represented in publication [6] listed above. This study demonstrated that a positive ion of charge Q and velocity v, incident on a Rydberg atom with principal quantum number n and binding energy $E_T$ captures a single electron into a narrow range of excited levels whose binding energies are somewhat greater than $E_T$. The ratio of most probable product binding energy, $E_P$, and $E_T$ was measured precisely across a range of Q from 1 to 11 and found to agree well with the predictions of Classical Trajectory Monte Carlo theory (CTMC) but disagree significantly with several common approximations. The width of the binding energy distribution was found to be given by

$$W\left(eV\right)\cong 1.5\,\frac{v(a.u.)}{\sqrt{Q}}\qquad 0.03\le\left(v\left(a.u.\right)\right)\le 0.13$$

The results of this extensive study are also reported in the PhD thesis of Daniel S. Fisher.

[T1] "Energy Transfer in Ion-Rydberg Charge Exchange" Dan Fisher (PhD, 2000, Colorado State Univ.)

In the course of these collision studies, it became apparent that the highly excited Rydberg ions formed in charge capture by HCI on the Rydberg target and detected with high spectral resolution through excitation by the Doppler-tuned $CO_2$ laser made possible a unique form of Rydberg ion spectroscopy. This in turn offered the opportunity to measure precisely certain properties of positive ions, such as polarizabilities and permanent electric moments, that could provide excellent tests of evolving atomic structure theories. Initial demonstrations of these capabilities was provided for ions with Q = 1,2, &3, and reported in publications 11-16 listed below.

[12] "Determination of the polarizability of Na-like Silicon by study of the fine structure of high-L Rydberg states of $Si^{2+}$", R.A. Komara, M.A. Gearba, S.R. Lundeen, and C.W. Fehrenbach, Phys. Rev A 67, 062502 (2003)

[13] "Indirect spin orbit interaction in high *L* Rydberg states with $^2S_{1/2}$ cores", E.L Snow, R.A. Komara, M.A. Gearba, and S.R. Lundeen, Phys. Rev. A 68, 022510(2003), Erratum, Phys. Rev. A 74, 049904(E) (2006)

[14] "Ion Properties from High-L Rydberg Fine Structure: Dipole Polarizability of $Si^{2+}$" R.A. Komara, M.A. Gearba, C.W. Fehrenbach, and S.R. Lundeen, J. Phys. B. At. Mol. Opt. Phys. 38, S87 (2005)

[15] "Determination of dipole and quadrupole polarizabilities of $Ba^+$ by measurement of the fine structure of high-L, n=9 and 10 Rydberg states of Barium" E.L. Snow, M.A. Gearba, W.G. Sturrus, and S.R. Lundeen, Phys. Rev A 71, 022510 (2005), Erratum Phys. Rev. A 74, 049905(E) (2006)

[16] "Fine Structure in High-L Rydberg states: A Path to Properties of Positive Ions" in Advances in Atomic, Molecular, and Optical Physics, Vol. 52 edited by Chun C. Lin and Paul Berman (Academic Press, 2005)

The unique capability demonstrated by these spectroscopic studies led to a change in objectives of this program in its renewal in 2005. It seemed reasonable to hope that if properties of positive ions with charge Q=1, 2, & 3 could be measured with this technique, it might also be possible to measure properties of ions with charge as high as 6. If this were possible, ions like the Rn-like and Fr-like ions of Th and U ($Th^{4+}$, $Th^{3+}$, $U^{6+}$, $U^{5+}$) could be studied, providing a unique and valuable test of theories predicting the properties of these ions, for which there were literally no experimental tests. Since these ions are common ionization states of Th and U in chemistry, testing predictions of the properties of the isolated ions could contribute to improved understanding of actinide chemistry. This became the new program goal, represented in the new program title:

**"Properties of Actinide Ions from Measurements of Rydberg Ion Fine Structure".**

The ultimate success of this program depended both on the development of the experimental techniques needed to measure reliably the fine structure patterns in Rydberg ions of high charge, and equally on improvements in the theoretical understanding of the connection between the measured patterns and the underlying positive ion propeerties. This led to a program divided into two parts.

**1)** At Kansas State University, efforts continued to extend the technique to higher charge Rydberg ions. As a first step, a study of Rydberg levels bound to the $Kr^{6+}$ ion was completed to demonstrate that ions with charge as high as 6 could be successfully studied. This is represented in publication [17].

[17] "Polarizability of $Kr^{6+}$ from High-L $Kr^{5+}$ Fine Structure Measurements", S.R. Lundeen and C.W. Fehrenbach, Phys. Rev. A 75, 032523 (2007)

Supported by this proof of principle, a new permanent magnet ECR Ion Source was purchased that was capable of producing the necessary beams of U and Th ions.

**2)** At Colorado State University, a program of parallel studies of neutral Rydberg levels bound to singly charged ions was pursued with the goal of extending and testing the theoretical framework connecting the observed fine structure patterns to the properties of the isolated positive ion cores. This evolved in two directions,

**a)** Extending the studies to core ions with higher values of angular momentum, whose fine structure patterns were increasingly complex. Since the $Th^{3+}$ and $U^{5+}$ ions have J=5/2, this represented a minimum goal. Eventually, high quality studies of Rydberg levels bound to $Ar^{+}$ (J=3/2) and $Ni^{+}$ (J=5/2) were successfully completed, as represented by publications 18-21 listed below.

[18] "Optical spectroscopy of high-L Rydberg states of Argon" L.E. Wright, E.L. Snow, S.R. Lundeen, and W.G. Sturrus, Phys. Rev. A 75, 022503 (2007)

[19] "Microwave spectroscopy of high-L, n=10 Rydberg states of Argon", M.E. Hanni, Julie A. Keele, W.G. Sturrus, and S.R. Lundeen, Phys. Rev. A 78, 062510 (2008)

[20] "Optical spectroscopy of high-L Rydberg states of nickel", Julie A. Keele, Shannon L. Woods, M.E. Hanni, S.R. Lundeen, and W.G. Sturrus, Phys. Rev. A 81, 022506 (2010)

[21] "Microwave Spectroscopy of high-*L*, *n*=9 Rydberg levels of Nickel: Polarizabilities and Moments of the $Ni^{+}$ ion", Shannon Woods, Chris Smith, Julie Keele, and S.R. Lundeen, Phys. Rev. A 87, 022511 (2013)

**b)** Testing the influence of higher-order corrections and non-adiabatic corrections to the fine structure patterns by studies of neutral Rydberg levels where these effects were significant. This is represented in publications 22-27 listed below.

[22] "Higher-order contributions to fine structure in high-L Rydberg states of $Si^{3+}$", E.L. Snow and S.R. Lundeen, Phys. Rev. A 75, 062512 (2007)

[23] "Fine Structure Measurements in high-L, n=17 and n=20 Rydberg states of Barium", E.L. Snow and S.R. Lundeen ,Phys. Rev. A, 76, 052505 (2007)

[24] "Determination of dipole and quadrupole polarizabilities of $Mg^{+}$ by fine structure measurements in high-L, n=17 Rydberg states of magnesium", E.L. Snow and S.R. Lundeen, Phys. Rev. A 77, 052501 (2008)

[25] "Dipole and quadrupole transition strengths in $Ba^{+}$ from measurements of K-splittings in high-L barium Rydberg levels", Shannon L. Woods, S.R. Lundeen, and Erica L. Snow, Phys. Rev. A 80, 042516 (2009)

[26] "Polarizabilities of $Pb^{2+}$ and $Pb^{4+}$ and Ionization Energies of $Pb^{+}$ and $Pb^{3+}$ from spectroscopy of high-*L* Rydberg states of $Pb^{+}$ and $Pb^{3+}$. M.E. Hanni, Julie A. Keele, S. R. Lundeen, C.W. Fehrenbach, and W.G. Sturrus, Phys. Rev. A 81, 042512 (2010)

[27] "Dipole transition strengths in $Ba^{+}$ from Rydberg fine structure measurements in Ba and $Ba^{+}$, Shannon L. Woods, M.E. Hanni, S.R. Lundeen, and Erica L. Snow, Phys. Rev. A 82, 012506 (2010)

Much of this work is represented in the PhD thesis of Erica Snow.

[T2] "Spectroscopy of High Angular Momentum Rydberg States with $^{2}S_{1/2}$ cores" Erica Snow (PhD, 2006, Colorado State University)

The culmination of much of this theoretical effort was the careful derivation of the form of the effective potential seen by the non-penetrating Rydberg electron bound to a positive ion of arbitrary angular momentum. This provides a rigorous foundation for studies extracting core ion properties from Rydberg fine structure measurements. It is reported in publication 28 listed below, and in the PhD thesis of Shannon Woods.

[28] "Effective Potential Model for high-L Rydberg atoms and ions" Shannon L. Woods and S.R. Lundeen, Phys. Rev. A 85, 042505 (2012)

[T3] "Ion Properties from High-L Rydberg atom spectroscopy: Application to Nickel", Shannon Woods (PhD, Colorado State University, 2012)

When Th and U ions became available from the new ECR source at Kansas State University in early 2009, the first experiments targeted the Rn-like $U^{6+}$ ion. These studies were expected to be similar in difficulty to the completed $Kr^{6+}$ experiment. In spite of a great deal of effort, no resolved fine structure signals were seen in these initial studies, and measurements showed that any signals were about an order of magnitude smaller than expected. In addition, a large background rate made measurement of small signals very time consuming. Frustrated by this lack of progress, a beam of the isoelectronic ion of Th, $Th^{4+}$ was obtained, and studies of Rydberg ions bound to this ion were begun. Almost immediately, a completely different result was obtained. In a few hours, useable data was obtained from which the dipole and quadrupole polarizabilites of the $Th^{4+}$ ion could be extracted. Furthermore, when a beam of the Fr-like $Th^{3+}$ ion was substituted for the $Th^{4+}$ ion, the much more complicated spectrum expected from this J=5/2 core ion was also seen without much difficulty, and analysis of the spectrum provided measurements of several properties of this f-electron Fr-like ion. These results are represented in publications 29 and 30 listed below, and in the PhD thesis of Mark Hanni.

[29] "Polarizabilities of Rn-like $Th^{4+}$ from spectroscopy of high-L Rydberg levels of $Th^{3+}$", M.E. Hanni, Julie A. Keele, S.R. Lundeen, and C.W. Fehrenbach, Phys. Rev. A 82, 022512 (2010)

[30] "Properties of Fr-like $Th^{3+}$ from spectroscopy of high-L Rydberg levels of $Th^{2+}$", Julie. A. Keele, M.E. Hanni, Shannon L. Woods, S.R. Lundeen , and C.W. Fehrenbach, Phys. Rev. A 83, 062501 (2011)

[T4] "Rydberg Spectroscopy of Fr-like Thorium and Uranium Ions", Mark Hanni (PhD, Colorado State University, 2010)

The studies of $Th^{4+}$ and $Th^{3+}$ were subsequently improved significantly using microwave spectroscopy, with results reported in publications 31-33 below, and in the PhD thesis of Julie Keele.

[31] "Polarizabilities of Rn-like $Th^{4+}$ from rf spectroscopy of $Th^{3+}$ Rydberg levels", Julie A. Keele, S.R. Lundeen, and C.W. Fehrenbach, Phys. Rev. A 83, 062509 (2011).

[32] "Measurements of dipole and quadrupole polarizabilities of Rn-like $Th^{4+}$", Julie. A. Keele, Chris S. Smith, S.R. Lundeen, and C.W. Fehrenbach, Phys. Rev. A 85, 064502 ( 2012)

[33] "Properties of Fr-like $Th^{3+}$ from rf spectroscopy of high-L $Th^{2+}$ Rydberg ions", Julie A. Keele, Chris Smith, S.R. Lundeen, and C.W. Fehrenbach, Phys Rev A 88, 022502 (2013)

[T5] "Properties of $Th^{4+}$ and $Th^{3+}$ from RF Spectroscopy of High-L Thorium Ions" Julie Keele (PhD, Colorado State University, 2013)

The ion properties obtained in these measurements provide a unique and detailed test of calculations of the properties of these two highly relativistic multi-electron ions. The table below illustrates some of these measured properties and compares them with theoretical calculations by several methods. It becomes apparent that only the most sophisticated relativistic theoretical methods can provide even modest accuracy for these properties.

| Ion and Property | Measurement | Prediction |
|---|---|---|
| $Th^{4+}$ : $\alpha_D$(a.u.) | 7.702(6)[a] | 7.699[c] (RCCSD(T)), 7.75[d] (RRPA), 8.96 (DF), 10.26 (HF) |
| $Th^{4+}$ : $\alpha_Q$ (a.u.) | 29.1(1.9)[a] | 28.8[d] (RRPA), 24.5 (DF) |
| $Th^{3+}$ : Q (a.u.) | 0.5931(14)[b] | 0.62[e] (RMBPT), 0.91 (DF) |
| $Th^{3+}$ : $\alpha_{D,0}$ (a.u.) | 15.224(33)[b] | 15.073[e] (RMBPT) |
| $Th^{3+}$ : $\alpha_{D,2}$ (a.u.) | -5.30(11)[b] | -6.166[e] (RMBPT) |
| $Th^{3+}$ : $\langle 5^2F_{5/2} \| M^{[1]} \| 6^2D_{3/2} \rangle$ | 1.436(2)[b] | 1.530[e] (RMBPT), 2.428 (DF) |
| $Th^{3+}$ : : $\langle 5^2F_{5/2} \| M[3] \| 6^2D_{5/2} \rangle$ | 3.3(1.1)[b] | 8.394[e] (RMBPT) |

a) This Project, Publication [32]

b) This Project, Publication [33]

c) Relativistic Couple Cluster, Schwerdtfeger and Borschevsky (Borschevsky, 2010)

d) Relativistic Random Phase Approximation, M. Safronova (Safronova M, 2010)

e) Relativistic Many Body Perturbation Theory, M. Safronova (Safronova M, 2010)

"DF", Dirac-Fock, "HF", Hartree-Fock

The successful completion of the studies of the Rn-like and Fr-like ions of Th, and the valuable quantitative tests that they provide of the theoretical descriptions of these important actinide ions, represent a satisfying conclusion of many years of effort towards an ambitious goal. Unfortunately, despite a great deal of effort, similar success was not achieved in the proposed studies of the isoelectronic ions of U. The final research goal of this project was to underrstand the reasons for this contrasting result, focussing in particular on the two Rn-like ions, $Th^{4+}$ and $U^{6+}$. Ultimately, a very credible explanation was found, involving a difference in the arrangement of the metastable excited levels in the first excited configuration of these ions. Both ions have a large number of metastable levels with one *6p* hole and a *5f* valence electron. These metastable Rn-like ions form metastable Rydberg ions when they capture a single electron in the Rydberg Target, and these metastable Rydberg ions can autoionize, producing the large background rates that make measurements of small signals difficult. This problem, however, is common to both ions and does not explain the contrasting results. The difference is traced to the fact that in $U^{6+}$, but <u>not</u> in $Th^{4+}$, the lowest energy metastable level is a J=1 level. The Rydberg ions bound to this J=1 level cannot autoionize by long-range electric quadrupole interactions, and are therefore effectively stable. These energetically metastable, but dynamically stable Rydberg ions contribute fully to the measured excitation signal, forming at least 75% of the signal and resulting in a very complex and very small signal that obscures the contributions of "normal" Rydberg ions bound to the $U^{6+}$ ground state. The evidence supporting this conclusion is presented in publication [34], now in preparation, and in the PhD thesis of Chris Smith.

[34] "Studies of Rn-like $Th^{4+}$ and $U^{6+}$ with the RESIS method", Chris Smith, S.R. Lundeen, and C.W. Fehrenbach (in Preparation)

[T6] "'Studies of $U^{6+}$ with the RESIS Method: Difficulties and Future Directions" Chris Smith (PhD, Colorado State University, 2015)