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RPPR Final Report
as of 13-Jan-2023

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Submitted By: Eric Hudson Email: ericrhudson@ucla.edu
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STEM Degrees: 2 **STEM Participants:** 2

Major Goals: See attached.

Accomplishments: See attached.

Training Opportunities: Nothing to Report

Results Dissemination: This DURIP award allowed us to purchase a laser system which has been used in a number of publications. The results have been presented at multiple conferences over the years and numerous invited talks.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

RPPR Final Report
as of 13-Jan-2023

Partners

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I certify that the information in the report is complete and accurate:
Signature: Eric Hudson
Signature Date: 1/11/23 4:56PM

A Laser System for Quantum Control of Chemical Reactions and Atom-Ion Photoassociation

Eric R. Hudson, UCLA

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Introduction

Our lab has recently developed two new tools, the hybrid atom-ion MOTION trap and an integrated time-of-flight mass spectrometer. Through this DURIP award we purchased a narrowband, tunable laser system, which in combination with these devices will allow us to probe two completely new areas of physics: quantum control of atom-ion chemical reactions and photoassociation of ultracold atoms and ions.

Using this laser system, we have been able to study several routes to full quantum control of chemical reactions, which should provide control of both the total reaction rate and the reaction products. Thus, this work has the potential to open up a new era in quantum control and state-to-state chemistry. Further, we expect that the control mechanisms demonstrated through this work will lay the framework for quantum control in more complicated systems, and as such could have impacts ranging from fundamental physics and chemistry to material science.

Using the same laser system, we also explored atom-ion photoassociation. Over the last decade, photoassociation of ultracold atoms has provided an enormous amount of information about molecular structure, and presently promises to revolutionize fields such as quantum chemistry, quantum information, and fundamental physics. Surprisingly, however, photoassociation studies have never been extended to atom-ion systems. With our recent development of the MOTION trap and the purchase of the laser system through DURIP, we were able to perform the first ever photoassociation studies of atoms and ions. We expect that this work will open a new area of research within AMO that will provide all of the benefits of photoassociation studies to atom-ion systems.

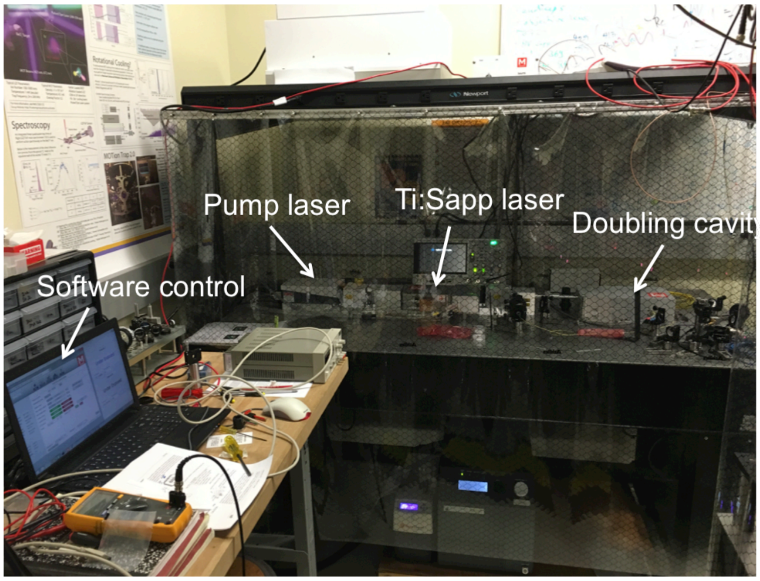
Finally, in addition to these two planned applications of the laser system, we also used the system in a plethora of experiments ranging from atomic spectroscopy and novel laser cooling to probing new types of molecular frameworks.

In what follows, we first describe the laser system and then briefly summarize the results made possible by the award.

Description of requested laser system and its use

The laser system is a tunable titanium sapphire, narrow band laser system with second harmonic generation capabilities from M squared Lasers LTD. This laser system is capable of generating wavelengths between 700 nm – 1000 nm when running without the frequency doubling capabilities and wavelengths between 350 nm – 500 nm when running with frequency doubling capabilities. This laser allows us to address the necessary wavelengths with the required tunability and laser intensity for reaction control and atom-ion photoassociation required by this project (~370 nm, 415, nm, 423 nm, and 493 nm). We also anticipate that this laser system will be come an integral tool for our laboratory in the years to come because of its flexibility.

The laser was installed in our laboratory earlier this year and is shown in the accompanying photographs.



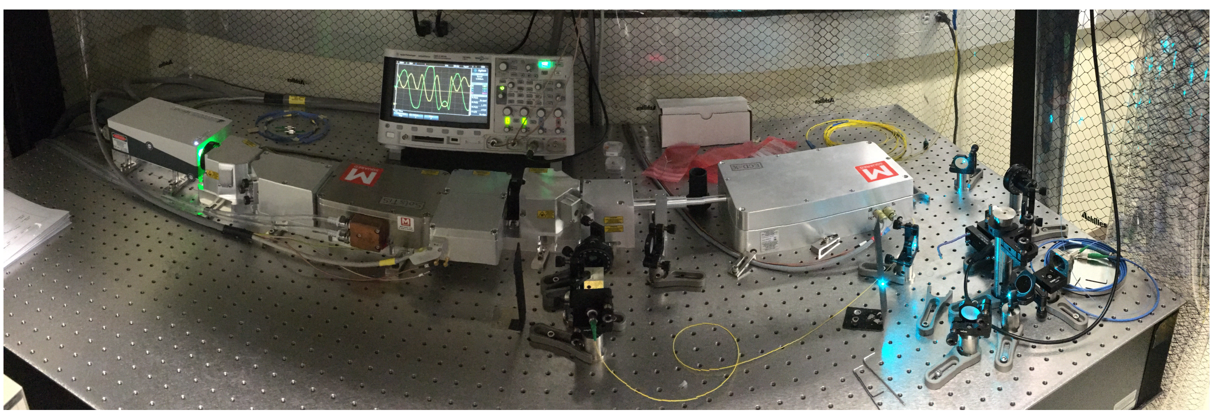


Fig. 1. (Top) Laser system layout. The laser was installed on a floating optical table inside a HEPA-filter-maintained atmosphere. The individual components of the laser, as well as its computer control are visible. This laser system is notoriously sensitive to vibrations, therefore it was installed on its own optical table and is fiber coupled to the rest of the experiment. (Bottom) Panoramic photograph of laser system in operation

Since the initial installation of the laser system, we have benchmarked its performance. We can achieve nearly 1 W of laser power at all of the doubled frequencies. We have also confirmed that the laser linewidth, when stabilized, is < 100 kHz. The achieved powers are:

	369 nm	389 nm	422 nm	493 nm	700-1000 nm
Power (mW)	750 mW	900 mW	1500 mW	750 mW	3000-4500 mW

Experiments enabled by this award

Since its installation this laser system has been an integral part of our laboratory and is constantly 'borrowed' by other UCLA researchers through the utilization of fiber interconnects installed between our laboratories. It has been involved in an 'uncountable' number of experiments, tests, and crazy ideas. In this section, we summarize publications from our group that involved the use of this laser system.

1. Functionalizing Aromatic Compounds with Optical Cycling Centers
Guo-Zhu Zhu, Debayan Mitra, Benjamin L. Augenbraun, Claire E. Dickerson, Michael J. Frim, Guanming Lao, Zack D. Lasner, Anastassia N. Alexandrova, Wesley C. Campbell, Justin R. Caram, John M. Doyle, and Eric R. Hudson.
Nature Chemistry (2022)

Molecular design principles provide guidelines for augmenting a molecule with a smaller group of atoms to realize a desired property or function. We demonstrate that these concepts can be used to create an optical cycling center that can be attached to a number of aromatic ligands, allowing the scattering of many photons from the resulting molecules without changing the molecular vibrational states. We provide further design principles that indicate the ability to expand this work. This represents a significant step towards a quantum functional group, which may serve as a generic qubit moiety that can be attached to a wide range of molecular structures and surfaces.

2. High-resolution laser-induced fluorescence spectroscopy of $^{28}Si^{16}O^+$ and $^{29}Si^{16}O^+$ in a cryogenic buffer-gas cell
Guo-Zhu Zhu, Guanming Lao, Clayton Ho, Wesley C. Campbell, and Eric R. Hudson.
J. Mol. Spectrosc. **384**, 111582 (2022)

The electronic, laser-induced fluorescence spectrum of the $B^2\Sigma^+ \leftarrow X^2\,\Sigma^+$ transition in $^{28}Si^{16}O^+$ and $^{29}Si^{16}O^+$ has been recorded in a cryogenic buffer gas cell at ≈ 100 K. Molecular constants are extracted for both $^{28}Si^{16}O^+$ and $^{29}Si^{16}O^+$, including the Fermi contact hyperfine constant for both the B and X states of $^{29}Si^{16}O^+$, and used in a discussion of the suitability of SiO^+ in future quantum information experiments.

3. Engineering Excited-State Interactions at Ultracold Temperatures
Mike Mills, Prateek Puri, Ming Li, Steven J. Schowalter, Alexander Dunning, Christian Schneider, Svetlana Kotochigova, and Eric R. Hudson
Phys. Rev. Lett. **122**, 233401 (2019)

Using a recently developed method for precisely controlling collision energy, we observe a dramatic suppression of inelastic collisions between an atom and ion (Ca +Yb^+) at low collision energy. This suppression, which is expected to be a universal phenomenon, arises when the spontaneous emission lifetime of the excited state is comparable to or shorter than the collision complex lifetime. We develop a technique to remove this suppression and engineer excited-state interactions. By dressing the system with a strong catalyst laser, a significant fraction of the collision complexes can be excited at a specified atom-ion separation. This technique allows excited-state collisions to be studied, even at ultracold temperature, and provides a general method for engineering ultracold excited-state interactions

4. Reaction blockading in a reaction between an excited atom and a charged molecule at low collision energy

Prateek Puri, Michael Mills, Ionel Simbotin, John A. Montgomergy Jr., Robin Cote, Christian Schneider, Arthur G. Suits, and Eric R. Hudson

Nature Chemistry **11**, 615 (2019)

Recent advances have enabled studies of atom–ion chemistry at unprecedentedly low temperatures, allowing precision observation of chemical reactions and novel chemical dynamics. So far, these studies have primarily involved reactions between atoms and atomic ions or non-polar molecular ions, often in their electronic ground state. Here, we extend this work by studying an excited atom–polar-molecular-ion chemical reaction ($Ca^* + BaCl^+$) at low temperature in a hybrid atom–ion trapping system. The reaction rate and product branching fractions are measured and compared to model calculations as a function of both atomic quantum state and collision energy. At the lowest collision energy we find that the chemical dynamics differ dramatically from capture theory predictions and are primarily dictated by the radiative lifetime of the atomic quantum state instead of the underlying excited-state interaction potential. This reaction blockading effect, which greatly suppresses the reactivity of short-lived excited states, provides a means for directly probing the reaction range and also naturally suppresses unwanted chemical reactions in hybrid trapping experiments.

5. High-resolution collision energy control through ion position modulation in atom-ion hybrid systems

Prateek Puri, Michael Mills, Elizabeth P. West, Christian Schneider, and Eric R. Hudson

Review of Scientific Instruments **89**, 083112 (2018)

We demonstrate an ion shuttling technique for high-resolution control of atom-ion collision energy by translating an ion held within a radio-frequency trap through a magneto-optical atom trap. The technique is demonstrated both experimentally and through numerical simulations, with the experimental results indicating control of ion kinetic energies from 0.05 to 1 K with a fractional resolution of ∼10 and the simulations demonstrating that kinetic energy control up to 120 K with a maximum predicted resolution of ∼100 is possible, offering order-of-magnitude improvements over most alternative techniques. Finally, we perform a proof-of-principle chemistry experiment using this technique and outline how the method may be refined in the future and applied to the study of molecular ion chemistry.

6. Synthesis of mixed hypermetallic oxide $BaOCa^+$ from laser-cooled reagents in an atom-ion hybrid trap

Prateek Puri, Michael Mills, Christian Schneider, Ionel Simbotin, John Montgomery, Robin Cote, Arthur Suits, and Eric R. Hudson
Science **357**, 1370 (2017)

Hypermetallic alkaline earth (M) oxides of formula MOM have been studied under plasma conditions that preclude insight into their formation mechanism. We present here the application of emerging techniques in ultracold physics to the synthesis of a mixed hypermetallic oxide, $BaOCa^+$. These methods, augmented by high-level electronic structure calculations, permit detailed investigation of the bonding and structure, as well as the mechanism of its formation via the barrierless reaction of Ca (^3P_J) with $BaOCH_3^+$. Further investigations of the reaction kinetics as a function of collision energy over the range 0.005 K to 30 K and of individual Ca fine-structure levels compare favorably with calculations based on long-range capture theory.

7. Efficent Repumping of a Ca magneto-optical trap
Michael Mills, Prateek Puri, Yanmei Yu, Andrei Derevianko, Christian Schneider, and Eric R. Hudson
Physical Review A **96**, 033402 (2017)

We investigate the limiting factors in the standard implementation of the Ca magneto-optical trap. We find that intercombination transitions from the $4s5p\,^1P_1$ state used to repump the electronic population from the $3d4s\,^1D_2$ state severely reduce the trap lifetime. We explore seven alternative repumping schemes theoretically and investigate five of them experimentally. We find that all five of these schemes yield a significant increase in the trap lifetime and consequently improve the number of atoms and peak atom density by as much as ∼20 times and ∼6 times, respectively. One of these transitions, at 453 nm, is shown to approach the fundamental limit for a Ca magneto-optical trap with repumping only from the dark $3d4s\,^1D_2$ state, yielding a trap lifetime of ∼5 s.

8. Blue-sky bifurcation of ion energies and the limits of neutral-gas sympathetic cooling of trapped ions
Steven J. Schowalter, Alexander J. Dunning, Kuang Chen, Prateek Puri, Christian Schneider, Eric R. Hudson

Nature Communications 7, 12448 (2016)
Sympathetic cooling of trapped ions through collisions with neutral buffer gases is critical to a variety of modern scientific fields, including fundamental chemistry, mass spectrometry, nuclear and particle physics, and atomic and molecular physics. Despite its widespread use over four decades, there remain open questions regarding its fundamental limitations. To probe these limits, here we examine the steady-state evolution of up to 10 barium ions immersed in a gas of three-million laser-cooled calcium atoms. We observe and explain the emergence of nonequilibrium behaviour as evidenced by bifurcations in the ion steady-state temperature,

parameterized by ion number. We show that this behavior leads to the limitations in creating and maintaining translationally cold samples of trapped ions using neutral-gas sympathetic cooling. These results may provide a route to studying non-equilibrium thermodynamics at the atomic level.

Summary

As evidenced by the above, this laser system has become an essential part of our laboratory. It has been involved in a number of high profile results appearing in top journals, e.g. Science, Nature Chemistry, and PRL, but perhaps more importantly its flexibility has allowed us to quickly test new ideas. As such, it has been a driver of innovation in our lab.

It has also been a useful tool to the larger AMO community at UCLA. For example, this recent paper (https://chemrxiv.org/engage/chemrxiv/article-details/636d495b924538918587fd39) is under review at Science and used this laser system for its data. In total, around 20 researchers have been trained on its operation.

Finally, while this might be somewhat out of place in a grant report, I cannot help but comment that we are extremely grateful for this DURIP award. This laser has been incredibly important to the development of many ideas in our lab and an integral piece of many noteworthy results. We sincerely appreciate that the ARO recognizes the need to support instrumentation at universities. These awards truly have a multiplicative effect.