REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)
10-02-2019

2. REPORT TYPE
Final Report

3. DATES COVERED (From - To)
1-Sep-2012 - 28-Feb-2018

4. TITLE AND SUBTITLE
Final Report: High-Resolution Quantum Control of Chemical Reactions

5a. CONTRACT NUMBER
W911NF-12-1-0476

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611103

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHORS

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

Yale University
Office of Sponsored Projects
25 Science Park - 3rd Floor
New Haven, CT 06520 -8327

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
61797-CH-MUR.120

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES
UU	UU	UU	UU	

19a. NAME OF RESPONSIBLE PERSON
David DeMille

19b. TELEPHONE NUMBER
203-432-3833

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

RPPR Final Report
as of 24-Apr-2019

Agency Code:

Proposal Number: 61797CHMUR **Agreement Number: W911NF-12-1-0476**

INVESTIGATOR(S):

Name: David P DeMille david.demi
Email: david.demille@yale.edu
Phone Number: 2034323833
Principal: Y

Organization: **Yale University**
Address: Office of Sponsored Projects, New Haven, CT 065208327
Country: USA

DUNS Number: 043207562 EIN: 060646973
Report Date: 31-May-2018 Date Received: 10-Feb-2019
Final Report for Period Beginning 01-Sep-2012 and Ending 28-Feb-2018
Title: High-Resolution Quantum Control of Chemical Reactions
Begin Performance Period: 01-Sep-2012 **End Performance Period:** 28-Feb-2018
Report Term: 0-Other
Submitted By: David DeMille Email: david.demille@yale.edu
Phone: (203) 432-3833
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 0 **STEM Participants:** 0

Major Goals: Our project had three major thrusts related to overall theme of High-Resolution Quantum Control of Chemical Reactions. These were:
1. Study of chemistry in the quantum degenerate regime (using molecules with temperatures below roughly one microKelvin, created by assembling ultracold atoms into diatomic species).
2. Improved methods of control in the cold regime (using molecules with temperatures in the regime of ~1 Kelvin)
3. Extending the species available in the ultracold (developing new methods for cooling into the milliKelvin regime or lower, and applicable to molecular species that have different chemical behavior than those that can be assembled out of atoms).

In thrust #1 (Chemistry in the quantum degenerate regime), our original set of goals included:
- Compute state-to-state reactions of K+KRb.
- Calculate collisions for dimer-dimer systems with full-rovibrational resolution, and investigate reactions mediated by van der Waals complexes.
- Compute potential energy surfaces (PES) for various atom/diatom+diatom systems (e.g., Li+LiH, LiYb+LiYb, etc.), and for ionic systems (e.g. Al^+ +H_2, Ca_2+Ca^+, etc.).
- Develop formalism and new methods to include hyperfine/long-range interactions, and external fields in molecular collisions, and solving large sets of coupled equations.
- Develop semiclassical theory interfaced with quantum defect theory (QDT) to produce observables.
- Produce LiNa Feshbach molecules in gas phase and in 3D optical lattices.
- Produce fermionic NaK Feshbach molecules in the gas phase starting from a degenerate Na-K Bose-Fermimixture.
- Optimize the formation efficiency of LiNa and NaK, and study inelastic collisions of both species.
- Identify suitable NaK excited states for STIRAP transfer to the rovibrational singlet ground state of NaK.
- Investigate Feshbach resonances in Yb+Li quantum degenerate mixtures, and LiYb Feshbach molecule formation in an optical trap and a 3D optical lattice.
- Investigate non-adiabatic effects and the geometric phase on ultracold reactions
- Incorporate electronic and nuclear spin dynamics during resonant collisions.
- Combine QDT, semiclassical theories, and coupled channels computational models.
- Use suitable LiNa and NaK excited states for STIRAP transfer to the vibrational ground state.
- Study of chemical reactions of LiNa in the ground state and suppression by Fermi statistics, and LiNa reactions with Na and Li atoms in different hyperfine states.
- Study of elastic and inelastic collisions of NaK molecules.
- Search for possible two-body bosonic bound pairs of Na2K2.

- Form deeply-bound LiYb molecules starting from LiYb Feshbach molecules.
- Study chemical reactivity of LiYb with Li, Yb , and LiYb, by varying temperature, density, lattice geometry, spin-polarization, and possibly electric dipole orientation.

In thrust #2 (Improved methods of control in the cold regime), our original goals included:

- Calculate long-range interactions between diatoms (electrostatic, dispersion, and induction terms) like LiYb, LiCa, etc., and explore how to control them with external fields.
- Develop frequency comb spectroscopy on cold samples of molecules.
- Demonstrate high resolution quantum control of molecular states.
- Demonstrate coherent population transfer in isolated molecules using stimulated Raman pumping pulses, and control of magnetic sublevels and M sublevel entanglement.
- Evaluate the role of anisotropies of long-range interactions in chemical reaction rates
- Demonstrate control of dynamic molecular wavepackets in translationally cold samples.
- Apply rapid adiabatic passage techniques to prepare targets for chemical reactions under single-collision conditions.

In thrust #3 (Extending the species available in the ultracold), our original goals included:

- Produce CaH and CaF beams to demonstrate their transverse laser cooling and slowing.
- Demonstrate magnetic trapping of CaH, and construct a microwave trap.
- Demonstrate magneto-optic trapping of SrF, transfer to a conservative trap, and observe SrF-SrF collisions.
- Demonstrate kW-scale long-pulse tunable laser and use it to apply stimulated laser slowing forces stronger than radiative force.
- Show 1D and 2D transverse laser cooling and magneto-optic trapping of a YO beam.
- Implement and demonstrate 3D cooling and trapping of YO molecules.
- Trap CaF in MOT and in a microwave trap, and observe CaF+CaF collisions.
- Co-trap Li with CaH, and observe Li+CaH collisions.
- Increase phase space density of SrF via sympathetic and/or evaporative cooling, and observe chemical reactions of trapped SrF.
- Use stimulated laser slowing for improved trap loading of SrF and/or trapping of other species.
- Use laser cooled and trapped YO molecules for dipolar collision studies.

Over the course of the project, these goals were modified somewhat to reflect new opportunities and developments in the field--largely due to our MURI team--as well as a few originally unanticipated difficulties. The resulting progress will be detailed in the Accomplishments section.

Accomplishments: See uploaded file.

Training Opportunities: This project provided support for 23 postdoctoral researchers, 51 Ph.D. students in physics and/or chemistry, and 3 undergraduate students during the past year. These students received mentoring from the project's faculty-level investigators in all aspects of their scientific training. This sort of research exposes students to a vast array of scientific methods and concepts. Experimentalists are trained to develop extensive skills and experience in areas such as numerical simulation and analysis; electronics design, construction and testing; computer-based data acquisition and analysis; laser, optical, and electro-optical operation and design; microwave and RF techniques; vacuum, gas handling and cryogenics; etc. Theorists develop thorough experience and training in both analytic and numerical methods that span atomic physics, chemical physics, and physical chemistry. At least 11 of the young researchers trained on this project now hold faculty positions. Most of the others remain in academia (continuing as grad students or postdocs in the field), but several have gone on to permanent positions in national laboratories (NIST, MIT Lincoln Labs) or industry.

RPPR Final Report
as of 24-Apr-2019

Results Dissemination: This grant resulted in 114 refereed publications, including many in the most prestigious journals: Science(5), Nature(5), Nature Phys.(2), Nature Chem.(1), and Phys. Rev. Lett. (18).

Our team gave over 100 invited presentations at conferences, workshops, and institutions. This included talks at the most prestigious conferences in the field such as the International Conference on Atomic Physics (3 talks); the International Conference on Laser Spectroscopy (2); American Physical Society DAMOP Meeting (5); APS March Meeting (2); American Chemical Society Annual Meeting (2); and the German Physical Society (DPG) Spring Meeting (3). We list these invited talks below. Graduate students and postdocs from our team also gave over 100 contributed presentations (in oral or poster format), not listed individually here.

J.Bohn:
Workshop on New Science with Ultracold Atoms, KITP, Santa Barbara, CA, 2013
Chemical Phys. Colloquium, JILA/Univ. of Colorado, 2013
AMO Phys. seminar, UCLA, 2013
Center for Ultracold Atoms (CUA) Seminar, Cambridge, MA, 2014
Frontiers of Cold Matter, Joint Quantum Inst. (JQI), College Park MD, 2014
Conf. on Cold and Controlled Molecules and Ions, Locarno, Switzerland, 2014
Workshop on The Few and the Many in Ultracold Physics, Orsay, France, 2014
Workshop on New Directions in Cold Chemical Physics, JILA, 2015
Dynamics of Molecular Collisions XXV, Asilomar, CA 2015
Center for Theory of Quantum Matter, JILA 2015

J. Ye:
ESF Workshop “Cold and Ultracold Molecules”, Obergurgl, Austria, 2012.
Phys. Colloquium, Univ. of Alabama, 2013
Phys. Colloquium, Univ. of Chicago, 2013
French-Israeli Conf. on Nonlinear and Quantum Optics, Ein Gedi, Israel, 2013
NEW SCIENCE WITH ULTRACOLD MOLECULES, KITP, 2013
Phys. Colloquium, Stony Brook Univ., NY, 2013
Phys. Colloquium, Univ. of Helsinki, 2013
Int'l Conf. on Laser Spectroscopy, Berkeley, CA, 2013
Int'l Conf. on Quantum Technologies, Moscow, Russia, 2013
Phys. Colloquium, Princeton Univ., NJ, 2014
DARPA New Science and Technologies Initiative, Washington D.C., 2014
OSU Lecture Series on Frontiers in Molecular Spectroscopy, Ohio State Univ., Columbus, 2014
Perspectives on ultracold atoms and molecules, Univ. of Maryland, 2014
Canadian Chemistry Conf. and Exhibition, Vancouver, 2014
Int' School of Physics Enrico Fermi, Varenna, Italy, 2014
(with D. S. Jin), Gordon Research Conf. on Quantum Science, Easton, MA 2014
Colloquium, Max Planck Inst. for Quantum Optics, Garching, Germany, 2014
Colloquium, Univ. of Hamburg, Germany, 2014
Colloquium, Inst. of Atomic and Molecular Sciences, Academia Sinica, Taipei, 2015
APS March Meeting, 2015
(with S. A. Moses, J. P. Covey, M. T. Miecnikowski, and D. S. Jin) Workshop on Quantum Many-Body Systems Far From Equilibrium, Nat'l Inst. for Theoretical Phys., Stellenbosch, South Africa, 2015
Aspen Winter Conf. Non-equilibrium quantum matter,2015
Colloquium, Int'l Solvay Insts., and Workshop on Atomic and Molecular Collision Mechanisms, Brussels, Belgium, 2015
Colloquium and OSA Traveling Lecture, Univ. of Virginia, 2015.
Workshop on Defining New Directions in Cold Chemical Physics, JILA, 2015
Colloquium on High-Resolution Molecular Spectroscopy, Dijon, France, 2015
US-Japan Joint Seminar on Quantum Electronics and Laser Spectroscopy, 2015
Frontiers in Optics / Laser Science, 2015
Phys. Colloquium, Univ. of Maryland, 2015
Colloquium, Inst. for Molecular Science, Okazaki, Japan 2016
German Physical Society Spring Meeting (DPG), Hannover, Germany, 2016
Lord Lecture of Modern Optics and Spectroscopy, MIT, 2016
Frontiers in Chemical Research Lecture, Texas A&M Univ., 2016

Scattering Workshop XIV, Trieste, Italy, 2017
(with B. Spaun) Workshop on Roaming & Cold Molecule Dynamics, Emory Univ., 2016
(with B. J. Bjork), APS March Meeting, 2017

S. Gupta:
Int'l Workshop on Group II Atoms, Nat'l Inst. of Information and Communications Technology, Tokyo, Japan, 2012
New Science with Ultracold Molecules Conf., KITP, 2013
2013 Workshop on Quantum Matter, Zhejiang University, Hangzhou, China. 2013
INT Workshop on Few-Body Physics, 2014
ICTS School & Discussion Meeting on Frontiers in Light-Matter Interactions, IACS, Kolkata, India, 2014
INT Workshop on Frontiers in Quantum Simulation with Cold Atoms, 2015
Int'l Workshop on Ultracold Group II Atoms, Paris Observatory, Paris, France, 2016
25th Int'l Conf. on Atomic Physics, Seoul, Korea, 2016

S. Kotochigova:
European Conf. on the Dynamics of Molecular Systems, Oxford, UK, 2012
Workshop on Fundamental Science and Applications of Ultracold Polar Molecules, KITP, 2013
Int'l Conf. on Quantum Reactive Scattering, , Bordeaux (France), 2013.
Colloquium, CSI, Madrid, Spain, 2013
Colloquium, Univ. of Granada, Spain 2013
Max-Planck-Inst. and LMU Colloquium, Munich, Germany, 2014
Wilhelm and Else Heraus Seminar 557, Germany, 2014
INT workshop, 2014
American Chemical Society meeting 2016
Workshop on Roaming and Cold Molecules, Emory University, 2016
Workshop on Impurities in Atomic and Molecular Systems, ITAMP, 2017.

B. Naduvalath:
APS DAMOP Meeting, Quebec, Canada, 2013.
Telluride Meeting on Intermolecular Interactions: New Challenges for Ab Initio Theory, 2013
A Symposium on Science@ITAMP,2014
From Atomic to Mesoscale: The Role of Quantum Coherence in Systems of Various Complexities, ITAMP, 2014
Int'l Workshop on Quantum Reactive Scattering, Salamanca, Spain, 2015
ICTS School and Discussion Meeting on Frontiers of Light-Matter Interactions, Kolkata, India, 2014
Int'l Conf. on Photodynamics and Related Aspects, Oaxaca, Mexico, 2014
Quantum Systems in Chemistry and Physics XXI, Univ. British Columbia, Vancouver, Canada 2016
Symposium on Chemical Kinetics and Dynamics, Saitama, Japan, 2016.
Colloquium, Univ. of Georgia, 2016
Pacifichem, 2015
Quantum Reactive Scattering Workshop XIV, Trieste, Italy, 2017

M. Zwierlein:
APS March Meeting, 2015
DPG Spring Meeting, Heidelberg, Germany, 2015
Pittsburgh Quantum Inst., 2016
Frontiers in Ultracold Fermi Gases, Florence, Italy, 2016
Cold and Controlled Molecules & Ions, Weizmann Inst., Rehovot, Israel, 2016
UQUAM Int’l Workshop on Ultracold Quantum Matter, Innsbruck, Austria, 2015
BEC 2015, Sant Feliu, Spain, 2015
APS DAMOP Meeting (I.I. Rabi Prize Talk), 2017
EGAS Conf., Durham, England 2017

J. Doyle:
Workshop: Defining New Directions in Cold Chemical Physics, JILA 2015
Phys. Seminar, Kyoto Univ., Japan, 2014
Phys. Seminar, Toyama Univ., Japan, 2014
Phys. Seminar, Nagoya, Univ., Japan, 2014
Phys. Seminar, Okayama Univ., Japan, 2014
Japan Conf. on Molecular Spectroscopy, Tokyo, 2014

Japan Conf. on Quantum Technology, Tokyo, 2014
Int'l Conf. on Atomic Physics, 2014
APS DAMOP Meeting, 2014
Int'l Symposium on Molecular Beams, Nijmegen, NL, 2017

D. DeMille:
ACS National Meeting, 2016 [given by D. McCarron]
Int’l Conf. on Atomic Physics, Seoul, Korea, 2016
Cold and Controlled Molecules and Ions Conf., Weizmann Inst., Israel, 2016
German Physical Society (DPG) Spring meeting, Hannover, 2016
Harvard Joint Quantum Sciences Seminar, 2016
OSA Traveling Lecturer Colloquium and Seminar, Univ. of San Luis Potosi, Mexico, 2015
U.S.-Japan Seminar on Many-Body Quantum Systems, Madison, WI, 2015
Special Seminar, IQOQI, Innsbruck, 2015
Special Seminar, Max Planck Inst. for Quantum Optics, Munich, 2015
Workshop “Defining New Directions in Cold Chemical Physics”, JILA, 2015
Int’l Conf. on Laser Spectroscopy, Singapore, 2015 (given by Daniel McCarron)
Pacific Conf. on Spectroscopy and Dynamics, 2015
Phys. Department Colloquium, Temple U., 2014
Atomic Phys. Seminar, Stanford U., 2014
JQI Seminar, 2014
APS DAMOP Meeting, 2014
R.B. Woodward Lecture in the Chemical Sciences, Harvard U., 2014
Chemistry Department “Club Med” Seminar, Yale U., 2014
APS DAMOP Meeting, Quebec, Canada, 2013
Harvard/MIT CUA Seminar, 2013
KITP Conf. on Ultracold Molecules, 2013
Atomic Phys. Seminar, Georgia Inst. of Technology, 2012

N. Mukherjee (with R. Zare and W. Perreault):
Dynamics of Molecular Collisions, Lake Tahoe, CA 2017

RPPR Final Report
as of 24-Apr-2019

Honors and Awards: PI Martin Zwierlein:
-William W. Buechner Teaching Prize, MIT, 2012
-Thomson Reuters Highly Cited Researcher (Top 1%)
-APS I.I. Rabi Prize in Atomic, Molecular and Optical Physics 2017
-Elected APS Fellow, 2016

PI J. Ye:
-Rocky Mountain Eagle Award, 2014
-Gold Medal, US Department of Commerce, 2014
-Thomson Reuters Highly Cited Researcher (Top 1%)
-Presidential Rank Award (US), Distinguished, for 2015
-Jacob Rabinow Award, National Institute of Standards and Technology, 2017

PI W. Ketterle:
Thomson Reuters Highly Cited Researcher (Top 1%)

Boerge Hemmerling (Postdoc, Harvard):
-Wissenschaftspreis Hannover, Freundeskreis der Leibniz Universitaet Hannover eV, University of Hannover, Germany.

Waseem Bakr (Postdoc, MIT):
-Infinite Kilometer (K) Award, MIT School of Science 2013

Sebastian Will (Postdoc, MIT) \
- Infinite Kilometer (K) Award, MIT School of Science 2014

Jennifer Schloss (Graduate Student, MIT):
-Hertz Fellowship 2013

Matthew Nichols (Graduate Student, MIT):
-NDSEG Fellowship 2013

Protocol Activity Status:

Technology Transfer: co-PI S. Kotochigova engaged in scientific discussions with Dr. Michael Foss-Feig of the Army Research Laboratory (Adelphi, MD), and in scientific collaboration and transfer of research results to Dr. B. Kendrick of Los Alamos National Laboratory, NM.

The Ketterle group (MIT) worked with M Squared Lasers to test and provide application notes for their 671nm Ti: Sapphire laser, which was used for photoassociation spectroscopy at MIT.

PARTICIPANTS:

Participant Type: Faculty
Participant: Ming Li
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Alex Petrov
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:

National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: James Croft
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.109.115303
Volume: 109 Issue: 11 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Optical Production of Stable Ultracold ^{88}Sr_{2} Molecules
Authors:
Keywords: Ultracold gases, trapped gases, Laser-modified scattering and reactions, Atoms in optical lattices, Trapping of molecules
Abstract: We have produced large samples of stable ultracold 88Sr2 molecules in the electronic ground state in an optical lattice. The fast, all-optical method of molecule creation involves a near-intercombination-line photoassociation pulse followed by spontaneous emission with a near-unity Franck-Condon factor. The detection uses excitation to a weakly bound electronically excited vibrational level corresponding to a very large dimer and yields a high-Q molecular vibronic resonance. This is the first of two steps needed to create deeply bound 88Sr2 for frequency metrology and ultracold chemistry.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.4790402
Volume: 138 Issue: 5 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Communication: Transfer of more than half the population to a selected rovibrational state of H2 by Stark-induced adiabatic Raman passage
Authors:
Keywords: Magneto-optical and electro-optical spectra and effects; Rotation, vibration, and vibration-rotation constants; Mass spectra; Line and band widths, shapes, and shifts; Photon interactions with molecules; Level crossing and optical pumping; Multiphoton ionization and excitation to highly excited states (e.g., Rydberg states)
Abstract: By using Stark-induced adiabatic Raman passage (SARP) with partially overlapping nanosecond pump (532 nm) and Stokes (683 nm) laser pulses, 73% ± 6% of the initial ground vibrational state population of H2 (v = 0, J = 0) is transferred to the single vibrationally excited eigenstate (v = 1, J = 0). In contrast to other Stark chirped Raman adiabatic passage techniques, SARP transfers population from the initial ground state to a vibrationally excited target state of the ground electronic surface without using an intermediate vibronic resonance within an upper electronic state. Parallel linearly polarized, co-propagating pump and Stokes laser pulses of respective durations 6 ns and 4.5 ns, are combined with a relative delay of ?4 ns before orthogonally intersecting the molecular beam of H2. The pump and Stokes laser pulses have fluences of ?10 J/mm2 and ?1 J/mm2, respectively. The intense pump pulse generates the necessary sweeping of the Raman resonance frequency by ac (second-order) Sta
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Submitted to Molecular Physics
Publication Identifier Type: Publication Identifier:
Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: On the transverse confinement of radiatively-slowed molecular beams
Authors:
Keywords: laser cooling; molecular beams; Stark and Zeeman effects
Abstract: Radiative forces from near-resonant laser light can be used for cooling and slowing the motion of diatomic molecules. While radiative-force slowing can be efficient in reducing the longitudinal velocity of molecules in a beam, this method has so far resulted in relatively low fluxes of slow molecules available for loading into a trap. This is primarily due to the divergence of the molecular beam, which increases in inverse proportion to the forward velocity. In this paper we discuss methods to transversely confine molecules as they are slowed by radiative forces. We focus in particular on a promising method that uses a microwave field in the TE01 mode of a cylindrical cavity, tuned to the blue of a rotational transition in the molecule, to provide the confining force. We argue that, with a realistic design, this approach can improve the useful flux of slow molecules from radiative slowing by a factor of ↑100.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: N **Publication Status:** 1-Published
Journal: arXiv:1301.4172v3; submitted to Phys. Rev. A
Publication Identifier Type: Publication Identifier:
Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: External field control of spin-dependent rotational decoherence of ultracold polar molecules
Authors:
Keywords: Trapping of molecules, Ultracold gases, trapped gases
Abstract: We determine trapping conditions for ultracold polar molecules, where pairs of internal states experience identical trapping potentials. Such conditions could ensure that detrimental effects of inevitable inhomogeneities across an ultracold sample are significantly reduced. In particular, we investigate the internal rovibronic and hyperfine quantum states of ultracold fermionic groundstate 40K87Rb polar molecules, when static magnetic, static electric, and trapping laser fields are simultaneously applied. Understanding the effect of changing the relative orientation or polarization of these three fields is of crucial importance for creation of decoherence-free subspaces built from two or more rovibronic states. Moreover, we evaluate the induced dipole moment of the molecule in the presence of these fields, which will allow control of interactions between molecules in different sites of an optical lattice and study the inuence of the interaction anisotropy on the ability to entangle pol
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Chemical Reviews
Publication Identifier Type: DOI Publication Identifier: 10.1021/cr200362u
Volume: 112 Issue: 9 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: The Buffer Gas Beam: An Intense, Cold, and Slow Source for Atoms and Molecules
Authors:
Keywords: molecular beams; cold molecules
Abstract: Beams of atoms and molecules are stalwart tools for spectroscopy and studies of collisional processes. The supersonic expansion technique can create cold beams of many species of atoms and molecules. However, the resulting beam is typically moving at a speed of 300–600 m/s in the laboratory frame and, for a large class of species, has insufficient flux (i.e., brightness) for important applications. In contrast, buffer gas beams can be a superior method in many cases, producing cold and relatively slow atoms and molecules in the laboratory frame with high brightness and great versatility. There are basic differences between supersonic and buffer gas cooled beams regarding particular technological advantages and constraints. At present, it is clear that not all of the possible variations on the buffer gas method have been studied. In this review, we will present a survey of the current state of the art in buffer gas beams, and explore some of the possible future directions that these new
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: N **Publication Status:** 1-Published
Journal: Submitted to J. Chem. Phys.
Publication Identifier Type: Publication Identifier:
Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Ultracold collisions of O(1D) and H2: The effects of H2 vibrational excitation on the production of vibrationally and rotationally excited OH
Authors:
Keywords: ultracold collisions; vibrational and rotational energies; reactive collisions
Abstract: A quantum dynamics study of the O(1D)+H2(v = 0?2, j = 0) system in its electronic ground state has been carried out using the potential energy surfaces of Dobbyn and Knowles [Mol. Phys. 91, 1107 (1997)]. A time-independent quantum mechanical method based on hyperspherical coordinates is adopted for the dynamics calculations. Energy dependent cross section, probability, and rate coefficients are computed for the elastic, inelastic, and reactive channels over collision energies ranging from the ultracold to thermal regimes and for total angular momentum quantum number J = 0. The effect of initial vibrational excitation of the H2 molecule on vibrational and rotational populations of the OH product is investigated as a function of the collision energy. Comparison of results for vibrational levels v = 0?2 of H2 demonstrates that the vibrational excitation of H2 and its non-reactive relaxation pathway play a minor role in the overall collisional outcome of O(1D) and H2. It is also found that
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.110.173203
Volume: 110 Issue: 0 First Page #: 173203
Date Submitted: 1/27/19 12:00AM Date Published: 4/25/13 4:00AM
Publication Location:
Article Title: Deviation from Universality in Collisions of Ultracold ^6Li_2 Molecules
Authors: Tout T. Wang, Myoung-Sun Heo, Timur M. Rvachov, Dylan A. Cotta, Wolfgang Ketterle
Keywords: Matter waves; Intermolecular and atom-molecule potentials and forces; Scattering of atoms and molecules; Degenerate Fermi gases
Abstract: Collisions of ^6Li_2 molecules reveal a striking deviation from universal predictions based on longrange van der Waals interactions. Li_2 closed-channel molecules are formed in the highest vibrational state near a narrow Feshbach resonance, and decay via two-body collisions with Li_2, Li, and Na. For Li_2+Li_2 and Li_2+Na, the decay rates agree with the universal predictions of the quantum Langevin model. In contrast, the rate for Li_2+Li is exceptionally small, with an upper bound ten times smaller than the universal prediction. This can be explained by the low density of available decay states in systems of light atoms [G. Qu´em´ener, J.-M. Launay, and P. Honvault, Phys. Rev. A 75, 050701 (2007)], for which such collisions have not been studied before.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 24-Apr-2019

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nature
Publication Identifier Type: DOI Publication Identifier: 10.1038/nature11718
Volume: 492 Issue: 7429 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Evaporative cooling of the dipolar hydroxyl radical
Authors:
Keywords: Ultracold gases
Abstract: Atomic physics was revolutionized by the development of forced evaporative cooling, which led directly to the observation of Bose–Einstein condensation1,2, quantum-degenerate Fermi gases3 and ultracold optical lattice simulations of condensed-matter phenomena4. More recently, substantial progress has been made in the production of cold molecular gases5. Their permanent electric dipole moment is expected to generate systems with varied and controllable phases6–8, dynamics9–11 and chemistry12–14. However, although advances have been made15 in both direct cooling and cold-association techniques, evaporative cooling has not been achieved so far. This is due to unfavourable ratios of elastic to inelastic scattering13 and impractically slow thermalization rates in the available trapped species. Here we report the observation of microwave-forced evaporative cooling of neutral hydroxyl (OH.) molecules loaded from a Stark-decelerated beam into an extremely high-gradient magnetic quadrupole trap
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.110.143001
Volume: 110 Issue: 14 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: 2D Magneto-Optical Trapping of Diatomic Molecules
Authors:
Keywords: Slowing and cooling of molecules; Trapping of molecules; Mechanical effects of light on atoms, molecules, and ions
Abstract: We demonstrate one- and two-dimensional transverse laser cooling and magneto-optical trapping of the polar molecule yttrium (II) oxide (YO). In a 1D magneto-optical trap (MOT), we characterize the magneto-optical trapping force and decrease the transverse temperature by an order of magnitude, from 25 to 2 mK, limited by interaction time. In a 2D MOT, we enhance the intensity of the YO beam and reduce the transverse temperature in both transverse directions. The approach demonstrated here can be applied to many molecular species and can also be extended to 3D.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Molecular Physics
Publication Identifier Type: DOI Publication Identifier: 10.1080/00268976.2013.793838
Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Electric-field-induced inelastic collisions between magnetically trapped hydroxyl radicals
Authors:
Keywords: inelastic collisions, hydroxyl (OH) radicals, cold molecules, non-adiabatic trap loss;
Abstract: Inelastic collisions are observed between magnetically trapped neutral hydroxyl (OH•) radicals at a temperature of 45 mK in the presence of an electric field. The collision rate is measured over a range of electric fields from 0.2 to 10 kV/cm. However, the two-body collision rates must be deconvolved from a novel electric-field induced non-adiabatic single particle loss, which arises from Landau–Zener crossings between energy surfaces at the plane where the electric field vector is transverse to the trapping magnetic field. The observed inelastic collision rate follows an approximate quadratic power law in the effective dipole moment.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.110.173202
Volume: 110 Issue: 17 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Spin-Orbit Suppression of Cold Inelastic Collisions of Aluminum and Helium
Authors:
Keywords: Scattering of atoms and molecules, Interatomic potentials and forces, Atom cooling methods
Abstract: We present a quantitative study of suppression of cold inelastic collisions by the spin-orbit interaction. We prepare cold ensembles of >1011 Al(2P1/2) atoms via cryogenic buffer-gas cooling and use a single-beam optical pumping method to measure their magnetic (mJ-changing) and fine-structure (J-changing) collisions with 3He atoms at millikelvin temperatures over a range of magnetic fields from 0.5 to 6 T. The experimentally determined rates are in good agreement with the functional form predicted by quantum scattering calculations using ab initio potentials. This comparison provides direct experimental evidence for a proposed model of suppressed inelasticity in collisions of atoms in 2P1/2 states [T.?V. Tscherbul et al., Phys. Rev. A 80 040701(R) (2009)], which may allow for sympathetic cooling of other 2P1/2 atoms (e.g., In, Tl and metastable halogens).
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Physical Review A

Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevA.88.012707

Volume: 88 Issue: 1 First Page #: 0

Date Submitted: Date Published:

Publication Location:

Article Title: Zeeman relaxation induced by spin-orbit coupling in cold antimony-helium collisions

Authors:

Keywords: Elastic; ultracold collisions, Interatomic potentials and forces

Abstract: We investigate Zeeman relaxation in cold Sb(4S3/2?)–He collisions in a magnetic field. Ensembles of >1013 laser-ablated Sb atoms are cooled in cryogenic 4He buffer gas to 800 mK and inelastic collisions are observed to equilibrate the mJ-state distribution to the translational temperature. The ratio ? of momentum transfer to inelastic collision rates is measured to be ?9.1×102. We also perform quantum scattering calculations of Sb–4He collisions, based on ab initio interaction potentials, that demonstrate significant anisotropy of the ground state induced by the spin-orbit interaction. Agreement is obtained between theory and experiment with a ? 10% increase in the ab initio potential depth. This work suggests that buffer-gas-cooled pnictogen atoms lighter than Sb can be loaded into a magnetic trap.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: The Journal of Chemical Physics

Publication Identifier Type: DOI Publication Identifier: 10.1063/1.4818526

Volume: 139 Issue: 7 First Page #: 0

Date Submitted: Date Published:

Publication Location:

Article Title: Optical preparation of H2 rovibrational levels with almost complete population transfer

Authors:

Keywords: excited states, ground states, hydrogen neutral molecules, molecule-photon collisions, optical pumping, population inversion, rotational-vibrational states, stimulated Raman scattering, visible spectra

Abstract: Using stimulated Raman adiabatic passage (SARP), it is possible, in principle, to transfer all the population in a rovibrational level of an isolated diatomic molecule to an excited rovibrational level. We use an overlapping sequence of pump (532 nm) and dump (683 nm) single-mode laser pulses of unequal fluence to prepare isolated H2 molecules in a molecular beam. In a first series of experiments we were able to transfer more than half the population to an excited rovibrational level [N. Mukherjee, W. R. Dong, J. A. Harrison, and R. N. Zare, J. Chem. Phys. 138(5), 051101-1–051101-4 (2013)]10.1063/1.4790402. Since then, we have achieved almost complete transfer (97% ± 7%) of population from the H2 (v = 0, J = 0) ground rovibrational level to the H2 (v = 1, J = 0) excited rovibrational level. An explanation is presented of the SARP process and how these results are obtained.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Nature

Publication Identifier Type: DOI Publication Identifier: 10.1038/nature11753

Volume: 491 Issue: 7425 First Page #: 0

Date Submitted: Date Published:

Publication Location:

Article Title: Low-temperature physics: A chilling effect for molecules

Authors:

Keywords: Physics

Abstract: Cold and ultracold molecules provide fertile grounds for scientific discoveries. A method of cooling polyatomic molecules has been demonstrated that will allow researchers to explore the vast potential of these entities.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Molecular Physics
Publication Identifier Type: DOI Publication Identifier: 10.1080/00268976.2013.793833
Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: On the transverse confinement of radiatively slowed molecular beams
Authors:
Keywords: laser cooling, molecular beams, Stark and Zeeman effects
Abstract: Radiative forces from near-resonant laser light can be used for cooling and slowing the motion of diatomic molecules. While radiative-force slowing can be efficient in reducing the longitudinal velocity of molecules in a beam, this method has so far resulted in relatively low fluxes of slow molecules available for loading into a trap. This is primarily due to the divergence of the molecular beam, which increases in inverse proportion to the forward velocity. In this paper, we discuss methods to transversely confine molecules as they are slowed by radiative forces. We focus in particular on a promising method that uses a microwave field tuned to the blue of a rotational transition in the molecule, to provide the confining force.We argue that with a realistic design, this approach can improve the useful flux of slow molecules from radiative slowing by a factor of 100.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.110.173203
Volume: 110 Issue: 17 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Deviation from Universality in Collisions of Ultracold ^{6}Li_{2} Molecules
Authors:
Keywords: Intermolecular and atom-molecule potentials and forces, Matter waves, Scattering of atoms and moledules, Degenerate Fermi gases
Abstract: Collisions of 6Li2 molecules with free 6Li atoms reveal a striking deviation from universal predictions based on long-range van der Waals interactions. Li2 closed-channel molecules are formed in the highest vibrational state near a narrow Feshbach resonance and decay via two-body collisions with Li2, Li, and Na. For Li2+Li2 and Li2+Na, the decay rates agree with the universal predictions of the quantum Langevin model. In contrast, the rate for Li2+Li is exceptionally small, with an upper bound 10 times smaller than the universal prediction. This can be explained by the low density of available decay states in systems of light atoms [G. Quéméner, J.-M. Launay, and P. Honvault, Phys. Rev. A 75 050701 (2007)], for which such collisions have not been studied before.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.109.085301
Volume: 109 Issue: 8 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Ultracold Fermionic Feshbach Molecules of ^{23}Na^{40}K
Authors:
Keywords: Ultracold gases, trapped gases, Degenerate Fermi gases, Scattering of atoms and molecules, Slowing and cooling of molecules
Abstract: We report on the formation of ultracold weakly bound Feshbach molecules of 23Na40K, the first fermionic molecule that is chemically stable in its absolute ground state. The lifetime of the nearly degenerate molecular gas exceeds 100 ms in the vicinity of the Feshbach resonance. The measured dependence of the molecular binding energy on the magnetic field demonstrates the open-channel character of the molecules over a wide field range and implies significant singlet admixture. This will enable efficient transfer into the singlet vibrational ground state, resulting in a stable molecular Fermi gas with strong dipolar interactions.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nature
Publication Identifier Type: DOI Publication Identifier: 10.1038/nature12483
Volume: 501 Issue: 7468 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Observation of dipolar spin-exchange interactions with lattice-confined polar molecules
Authors:
Keywords: Ultracold molecules, dipolar interactions, optical lattices
Abstract: With the production of polar molecules in the quantum regime1, 2, long-range dipolar interactions are expected to facilitate understanding of strongly interacting many-body quantum systems and to realize lattice spin models3 for exploring quantum magnetism. In ordinary atomic systems, where contact interactions require wavefunction overlap, effective spin interactions on a lattice can be mediated by tunnelling, through a process referred to as superexchange; however, the coupling is relatively weak and is limited to nearest-neighbour interactions4, 5. In contrast, dipolar interactions exist even in the absence of tunnelling and extend beyond nearest neighbours. This allows coherent spin dynamics to persist even for gases with relatively high entropy and low lattice filling. Measured effects of dipolar interactions in ultracold molecular gases have been limited to the modification of inelastic collisions and chemical reactions6, 7. Here we use dipolar interactions of polar molecules pin
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Annual Review of Physical Chemistry
Publication Identifier Type: DOI Publication Identifier: 10.1146/annurev-physchem-040513-103744
Volume: 65 Issue: 1 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Cold State-Selected Molecular Collisions and Reactions
Authors:
Keywords: Cold Molecular Collsions, Cold Chemical Reactions
Abstract: Over the past decade, and particularly the past five years, a quiet revolution has been building at the border between atomic physics and experimental quantum chemistry. The rapid development of techniques for producing cold and even ultracold molecules without a perturbing rare-gas cluster shell is now enabling the study of chemical reactions and scattering at the quantum scattering limit with only a few partial waves contributing to the incident channel. Moreover, the ability to perform these experiments with nonthermal distributions comprising one or a few specific states enables the observation and even full control of state-to-state collision rates in this computation-friendly regime: This is perhaps the most elementary study possible of scattering and reaction dynamics.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.112.070404
Volume: 112 Issue: 7 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Suppressing the Loss of Ultracold Molecules Via the Continuous Quantum Zeno Effect
Authors:
Keywords: Tunneling traversal time quantum Zeno dynamics, Atoms in optical lattices, Trapping of molecules, Ultracold gases trapped gases
Abstract: We investigate theoretically the suppression of two-body losses when the on-site loss rate is larger than all other energy scales in a lattice. This work quantitatively explains the recently observed suppression of chemical reactions between two rotational states of fermionic KRb molecules confined in one-dimensional tubes with a weak lattice along the tubes [Yan et al., Nature (London) 501, 521 (2013)]. New loss rate measurements performed for different lattice parameters but under controlled initial conditions allow us to show that the loss suppression is a consequence of the combined effects of lattice confinement and the continuous quantum Zeno effect. A key finding, relevant for generic strongly reactive systems, is that while a single-band theory can qualitatively describe the data, a quantitative analysis must include multiband effects. Accounting for these effects reduces the inferred molecule filling fraction by a factor of 5. A rate equation can describe much of the data, but
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.112.033201
Volume: 112 Issue: 3 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Ultracold Heteronuclear Mixture of Ground and Excited State Atoms
Authors:
Keywords: Interatomic potentials and forces, Electric and magnetic moments polarizability, Elastic, ultracold collisions, Atom cooling methods
Abstract: We report on the realization of an ultracold mixture of lithium atoms in the ground state and ytterbium atoms in an excited metastable (P 2 3) state. Such a mixture can support broad magnetic Feshbach resonances which may be utilized for the production of ultracold molecules with an electronic spin degree of freedom, as well as novel Efimov trimers. We investigate the interaction properties of the mixture in the presence of an external magnetic field and find an upper limit for the background interspecies two-body inelastic decay coefficient of K ? 2 <3×10 ?12 ??cm 3 /s for the P 2 3 m J =?1 substate. We calculate the dynamic polarizabilities of the Yb(P 2 3) magnetic substates for a range of wavelengths, and find good agreement with our measurements at 1064 nm. Our calculations also allow the identification of magic frequencies where Yb ground and metastable states are identically trapped and the determination of the interspecies van der Waals coefficients.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.4865131
Volume: 140 Issue: 7 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Coherent superposition of M-states in a single rovibrational level of H2 by Stark-induced adiabatic Raman passage
Authors:
Keywords: stimulated Raman adiabatic passage; molecular alignment; molecular hydrogen
Abstract: We prepare an ensemble of isolated rovibrationally excited (v = 1, J = 2) H2 molecules in a phase-locked superposition of magnetic sublevels M using Stark-induced adiabatic Raman passage with linearly polarized single-mode pump (at 532 nm, ?6 ns pulse duration, 200 mJ/pulse) and Stokes (699 nm, ?4 ns pulse duration, 20 mJ/pulse) laser excitation. A biaxial superposition state, given by [line]?(t)? = 1/?(2)[[line]? = 1, J = 2, M = -2? - [line]? = 1, J = 2, M = +2?], is prepared with linearly but cross-polarized pump and Stokes laser pulses copropagating along the quantization z-axis. The degree of phase coherence is measured by using the O(2) line of the H2 E,F-X (0,1) band via 2 + 1 resonance enhanced multiphoton ionization (REMPI) at 210.8 nm by recording interference fringes in the REMPI signal in a time-of-flight mass spectrometer as the direction of the UV laser polarization is rotated using a half-wave plate. Nearly 60% population transfer from H2 (v = 0, J = 0) ground state to th
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.4830398
Volume: 139 Issue: 19 First Page #: 194305
Date Submitted: Date Published:
Publication Location:
Article Title: Chemical reaction versus vibrational quenching in low energy collisions of vibrationally excited OH with O
Authors:
Keywords: Hydrogen reactions, Collision induced chemical reactions, Trajectory models, Angular momentum, Basis sets
Abstract: Quantum scattering calculations are reported for state-to-state vibrational relaxation and reactive scattering in O + OH(v = 2 ? 3, j = 0) collisions on the electronically adiabatic ground state 2 A?? potential energy surface of the HO2 molecule. The time-independent Schrödinger equation in hyperspherical coordinates is solved to determine energy dependent probabilities and cross sections over collision energies ranging from ultracold to 0.35 eV and for total angular momentum quantum number J = 0. A J-shifting approximation is then used to compute initial state selected reactive rate coefficients in the temperature range T = 1 ? 400 K. Results are found to be in reasonable agreement with available quasiclassical trajectory calculations. Results indicate that rate coefficients for O2 formation increase with increasing the OH vibrational level except at low and ultralow temperatures where OH(v = 0) exhibits a slightly different trend. It is found that vibrational relaxation of OH in v =
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Physics B: Atomic, Molecular and Optical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1088/0953-4075/47/13/135202
Volume: 47 Issue: 13 First Page #: 135202
Date Submitted: Date Published:
Publication Location:
Article Title: Quantum dynamics of O(1D)+D2: isotopic and vibrational excitation effects
Authors:
Keywords: Atom and radical reactions; chain reactions; molecule-molecule reactions; Potential energy surfaces for chemical reactions; Rotation, vibration, and vibration-rotation constants; State selected dynamics and product distribution
Abstract: The effect of initial vibrational excitation of the D2 molecule on the quantum dynamics of the O(1D)+D2 reaction is investigated as a function of collision energy. The potential energy surface of Dobbyn and Knowles (1997 Mol. Phys. 91 1107) and a time-independent quantum mechanical method based on hyperspherical coordinates have been adopted for the dynamics calculations. Results for elastic, inelastic, and reactive scattering over collision energies ranging from the ultracold to thermal regimes are reported for total angular momentum quantum number J = 0. Calculations show that the collisional outcome of the O(1D)+D2 reaction is not strongly influenced by the initial vibrational excitation of the D2 molecule similar to its H2 counterpart. A J-shifting approximation is used to calculate the initial state selected reactive rate coefficients over the temperature range T = 1 ? 500 K. The reactive rate coefficients for D2(v = 0) are found to be in excellent agreement with available experim
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: New Journal of Physics
Publication Identifier Type: DOI Publication Identifier: 10.1088/1367-2630/16/6/063070
Volume: 16 Issue: 6 First Page #: 63070
Date Submitted: Date Published:
Publication Location:
Article Title: Buffer gas loaded magneto-optical traps for Yb, Tm, Er and Ho
Authors:
Keywords: Zeeman and Stark effects; Atom cooling methods

Abstract: Direct loading of lanthanide atoms into magneto-optical traps (MOTs) from a very slow cryogenic buffer gas beam source is achieved, without the need for laser slowing. The beam source has an average forward velocity of 60–$70\;{\rm m}\;{{{\rm s}}^{-1}}$ and a velocity half-width of $\sim 35\;{\rm m}\;{{{\rm s}}^{-1}}$, which allows for direct MOT loading of Yb, Tm, Er and Ho. Residual helium background gas originating from the beam results in a maximum trap lifetime of about 80 ms (with Yb). The addition of a single-frequency slowing laser applied to the Yb in the buffer gas beam increases the number of trapped Yb atoms to $1.3\left(0.7 \right)\times {{10}^{8}}$ with a loading rate of $2.0\left(1.0 \right)\times {{10}^{10}}\;{\rm atoms}\;{{{\rm s}}^{-1}}$. Decay to metastable states is observed for all trapped species and decay rates are measured. Extension of this approach to the loading of molecules into a MOT is discussed.

Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.4885363
Volume: 141 Issue: 1 First Page #: 14309
Date Submitted: Date Published:
Publication Location:
Article Title: Action spectroscopy of SrCl+ using an integrated ion trap time-of-flight mass spectrometer
Authors:
Keywords: Photodissociation; Molecular spectroscopy; Time of flight mass spectrometry; Electric dipole moments; Ab initio calculations

Abstract: The photodissociation cross-section of SrCl+ is measured in the spectral range of 36?000–46?000 cm?1 using a modular time-of-flight mass spectrometer (TOF-MS). By irradiating a sample of trapped SrCl+ molecular ions with a pulsed dye laser, X1?+ state molecular ions are electronically excited to the repulsive wall of the A1? state, resulting in dissociation. Using the TOF-MS, the product fragments are detected and the photodissociation cross-section is determined for a broad range of photon energies. Detailed ab initio calculations of the SrCl+ molecular potentials and spectroscopic constants are also performed and are found to be in good agreement with experiment. The spectroscopic constants for SrCl+ are also compared to those of another alkaline earth halogen, BaCl+, in order to highlight structural differences between the two molecular ions. This work represents the first spectroscopy and ab initio calculations of SrCl+.

Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nature
Publication Identifier Type: DOI Publication Identifier: 10.1038/nature13137
Volume: 507 Issue: 7493 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Quantum chaos in ultracold collisions of gas-phase erbium atoms
Authors:
Keywords: Techniques and instrumentation; Statistical physics; Quantum physics; Ultracold gases
Abstract: Atomic and molecular samples reduced to temperatures below one microkelvin, yet still in the gas phase, afford unprecedented energy resolution in probing and manipulating the interactions between their constituent particles. As a result of this resolution, atoms can be made to scatter resonantly on demand, through the precise control of a magnetic field1. For simple atoms, such as alkalis, scattering resonances are extremely well characterized2. However, ultracold physics is now poised to enter a new regime, where much more complex species can be cooled and studied, including magnetic lanthanide atoms and even molecules. For molecules, it has been speculated3, 4 that a dense set of resonances in ultracold collision cross-sections will probably exhibit essentially random fluctuations, much as the observed energy spectra of nuclear scattering do5. According to the Bohigas–Giannoni–Schmit conjecture, such fluctuations would imply chaotic dynamics of the underlying classical motion driving
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nature
Publication Identifier Type: DOI Publication Identifier: 10.1038/nature13634
Volume: 512 Issue: 7514 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Magneto-optical trapping of a diatomic molecule
Authors:
Keywords: Atomic and molecular interactions with photons; Ultracold gases
Abstract: Laser cooling and trapping are central to modern atomic physics. The most used technique in cold-atom physics is the magneto-optical trap (MOT), which combines laser cooling with a restoring force from radiation pressure. For a variety of atomic species, MOTs can capture and cool large numbers of particles to ultracold temperatures (less than ~1 millikelvin); this has enabled advances in areas that range from optical clocks to the study of ultracold collisions, while also serving as the ubiquitous starting point for further cooling into the regime of quantum degeneracy. Magneto-optical trapping of molecules could provide a similarly powerful starting point for the study and manipulation of ultracold molecular gases. The additional degrees of freedom associated with the vibration and rotation of molecules, particularly their permanent electric dipole moments, allow a broad array of applications not possible with ultracold atoms1. Spurred by these ideas, a variety of methods has been dev
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review A
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevA.89.021601
Volume: 89 Issue: 2 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Quenching to unitarity: Quantum dynamics in a three-dimensional Bose gas
Authors:
Keywords: Ultracold gases trapped gases, Matter waves, Boson degeneracy
Abstract: We study the dynamics of a zero-temperature Bose condensate following a sudden quench of the scattering length from noninteracting to unitarity (infinite scattering length). We apply three complementary approaches to understand the momentum distribution and loss rate. First, using a time-dependent variational ansatz for the many-body state, we calculate the dynamics of the momentum distribution. Second, we demonstrate that, at short times and large momenta compared to those set by the density, the physics can be understood within a simple, analytic two-body model. We make a quantitative prediction for the evolution of Tan's contact and find features in the momentum distribution that are absent in equilibrium. Third, we study three-body loss at finite density under the same dynamic scenario. We find lifetimes that are long compared to the saturation times of large-momentum modes, and we relate this result to the three-body inelasticity parameter.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: New Journal of Physics
Publication Identifier Type: DOI Publication Identifier: 10.1088/1367-2630/aa6470
Volume: 19 Issue: First Page #: 033035
Date Submitted: 1/27/19 12:00AM Date Published: 3/1/17 6:49AM
Publication Location:
Article Title: One dimensional magneto-optical compression of a cold CaF molecular beam
Authors: Eunmi Chae, Loic Anderegg, Benjamin L Augenbraun, Aakash Ravi, Boerge Hemmerling, Nicholas R H
Keywords: laser cooling, ultracold molecules, magneto-optical forces
Abstract: We demonstrate with a RF-MOT the one dimensional, transverse magneto-optical compression of a cold beam of calcium monofluoride (CaF). By continually alternating the magnetic field direction and laser polarizations of the magneto-optical trap, a photon scattering rate of 2├×0.4 MHz is achieved. A 3D model for this RF-MOT, validated by agreement with data, predicts a 3D RF-MOT capture velocity for CaF of 5 m/s.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Science Advances
Publication Identifier Type: DOI Publication Identifier: 10.1126/sciadv.aap8308
Volume: 4 Issue: 2 First Page #: eaap8308
Date Submitted: 1/27/19 12:00AM Date Published: 2/16/18 5:00AM
Publication Location:
Article Title: Fractal universality in near-threshold magnetic lanthanide dimers
Authors: Constantinos Makrides, Ming Li, Eite Tiesinga, Svetlana Kotochigova
Keywords: ultracold molecules; non-ergodic behavior; lanthanide molecules; fractal dimensions
Abstract: Ergodic quantum systems are often quite alike, whereas nonergodic, fractal systems are unique and display characteristic properties. We explore one of these fractal systems, weakly bound dysprosium lanthanide molecules, in an external magnetic field. As recently shown, colliding ultracold magnetic dysprosium atoms display a soft chaotic behavior with a small degree of disorder. We broaden this classification by investigating the generalized inverse participation ratio and fractal dimensions for large sets of molecular wave functions. Our exact close-coupling simulations reveal a dynamic phase transition from partially localized states to totally delocalized states and universality in its distribution by increasing the magnetic field strength to only a hundred Gauss (or 10 mT). Finally, we prove the existence of nonergodic delocalized phase in the system and explain the violation of ergodicity by strong coupling between near-threshold molecular states and the nearby continuum.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.121.113401
Volume: 121 Issue: 11 First Page #: 113401
Date Submitted: 1/27/19 12:00AM Date Published: 9/11/18 8:00AM
Publication Location:
Article Title: Unraveling the Stereodynamics of Cold Controlled HD - H_2 Collisions
Authors: James F.E. Croft, Naduvalath Balakrishnan, Meng Huang, Hua Guo
Keywords: Chemical reactions, Cold and ultracold molecules, Cooling & trapping, Ultracold collisions
Abstract: Measuring inelastic rates with partial-wave resolution requires temperatures close to a Kelvin or below, even for the lightest molecule. In a recent experiment, Perreault, Mukherjee, and Zare [Nat. Chem. 10, 561 (2018).] studied collisional relaxation of excited HD molecules in the v=1, j=2 state by para- and ortho-H2 at a temperature of about 1 K, extracting the angular distribution of scattered HD in the v=1, j=0 state. By state preparation of the HD molecules, control of the angular distribution of scattered HD was demonstrated. Here, we report a first-principles simulation of that experiment which enables us to attribute the main features of the observed angular distribution to a single L=2 partial-wave shape resonance. Our results demonstrate important stereodynamical insights that can be gained when numerically exact quantum scattering calculations are combined with experimental results in the few-partial-wave regime.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review A
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevA.96.062707
Volume: 96 Issue: 6 First Page #:
Date Submitted: 1/27/19 12:00AM Date Published: 12/18/17 5:00AM
Publication Location:
Article Title: Long-lived complexes and signatures of chaos in ultracold K_2+Rb collisions
Authors: J. F. E. Croft, N. Balakrishnan, B. K. Kendrick
Keywords: Atomic & molecular collisions; Scattering of atoms, molecules, clusters & ions; Ultracold collisions
Abstract: Lifetimes of complexes formed during ultracold collisions are of current experimental interest as a possible cause of trap loss in ultracold gases of alkali-metal dimers. Microsecond lifetimes for complexes formed during ultracold elastic collisions of K_2 with Rb are reported, from numerically exact quantum-scattering calculations. Thermally averaged lifetimes are compared with those calculated using a simple density-of-states approach, which are shown to be reasonable. This validates the density-of-states approach and suggests that the formation of long-lived complexes is indeed the cause of observed experimental trap loss in ultracold alkali-metal-dimer systems. Long-lived complexes correspond to narrow scattering resonances which we examine for the statistical signatures of quantum chaos, finding that the positions and widths of the resonances are in good agreement with the Wigner-Dyson and Porter-Thomas distributions, respectively.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.4998226
Volume: 147 Issue: 7 First Page #: 074302
Date Submitted: 1/27/19 12:00AM Date Published: 8/15/17 12:00PM
Publication Location:
Article Title: Symmetry and the geometric phase in ultracold hydrogen-exchange reactions
Authors: J. F. E. Croft, J. Hazra, N. Balakrishnan, B. K. Kendrick
Keywords: Particle symmetry, Geometric phases, Exchange reactions, Identical particles, Transition state, Reaction rate constants, Chemical elements, Quantum reactive scattering, Collision energies
Abstract: Quantum reactive scattering calculations are reported for the ultracold hydrogen-exchange reaction and its non-reactive atom-exchange isotopic counterparts, proceeding from excited rotational states. It is shown that while the geometric phase (GP) does not necessarily control the reaction to all final states, one can always find final states where it does. For the isotopic counterpart reactions, these states can be used to make a measurement of the GP effect by separately measuring the even and odd symmetry contributions, which experimentally requires nuclear-spin final-state resolution. This follows from symmetry considerations that make the even and odd identical-particle exchange symmetry wavefunctions which include the GP locally equivalent to the opposite symmetry wavefunctions which do not. It is shown how this equivalence can be used to define a constant which quantifies the GP effect and can be obtained solely from experimentally observable rates. This equivalence reflects...
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 5-Submitted
Journal: Science Advances (Submitted)
Publication Identifier Type: Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 1/27/19 12:00AM Date Published:
Publication Location:
Article Title: Unconventional chemistry with laser coolable SrOH polyatomic molecules
Authors: Ming Li, Jacek Klos, Alexander Petrov, Svetlana Kotochigova
Keywords: potential energy surfaces, laser cooling, akaline earth, hydroxyl, radical
Abstract: We used electronic structure methods to determine the ♀first few lowest two-dimensional potential energy surfaces (PESs) arising from the interaction between an alkaline-earth Sr atom and a hydroxyl radical. This interaction leads to a formation of the stable and collinear SrOH(X2\Sigma^+) radical used recently in successful laser cooling experiments. To characterize the SrOH molecule we employed a set of ab initio tools ranging from multi-reference con♀figuration interaction (MRCI) to equation-of-motion coupled-cluster methods with single and double excitations (EOM-CCSD) and the coupled cluster method with single and double excitations augmented with perturbatively calculated triples (CCSD(T)). The Sr+OH complex exhibits deep potential well corresponding to the ground electronic state of the SrOH radical. The ground state potential couples non-adiabatically with other close lying higher electronic states of the SrOH leading to signifi♀cant non-Born Oppenheimer character...
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review A
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevA.98.043423
Volume: 98 Issue: 4 First Page #: 043423
Date Submitted: 1/27/19 12:00AM Date Published: 10/16/18 4:00AM
Publication Location:
Article Title: Continuous production of rovibronic-ground-state RbCs molecules via short-range photoassociation to the b ^3?_1–c ^3?^+_1–B ^1?_1 states
Authors: Toshihiko Shimasaki, Jin-Tae Kim, Yuqi Zhu, David DeMille
Keywords: ultracold molecules, photoassociation
Abstract: We have investigated rovibronic levels of the strongly mixed b ^3?_1–c ^3?^+_1–B ^1?_1 states [the 2 (1), 3(1), and 4(1) states in Hund's case (c) notation] of 85Rb133Cs in the energy range of 13 950–14 200 cm^?1 using short-range photoassociation (PA). For selected PA states, vibrational and rotational branching in the X^1? ^+ state have been investigated using resonance-enhanced multiphoton ionization and depletion spectroscopy. Efficient production of 85Rb133Cs molecules in the rovibronic-ground-state (v=0,J=0), at up to ?1×10^4 molecules/s, has been achieved.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 3-Accepted
Journal: Review of Scientific Instruments
Publication Identifier Type: Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 1/27/19 12:00AM Date Published:
Publication Location:
Article Title: Injection-locking of a fiber-pigtailed laser to an external cavity diode laser via fiber optic circulator
Authors: Toshihiko Shimasaki, Eustace R. Edwards, David DeMille
Keywords: injection locking, fiber optic circulator, tunable laser
Abstract: We report a simple tunable master-slave laser injection-lock scheme for atomic physics experiments. Seed light from an external cavity diode laser is injected into a high-power fiber-pigtailed diode laser via a fiber optic circulator. High-power outputs (up to ?600 mW) at the injected frequency have been obtained in a single mode fiber with tuning over a wide wavelength range (?15 nm). The scheme is simpler and more cost-effective than the traditional scheme of free-space injection locking.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Chemistry Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1039/C7CP08481A
Volume: 20 Issue: 7 First Page #: 4739
Date Submitted: 2/6/19 12:00AM Date Published:
Publication Location:
Article Title: Two-photon spectroscopy of the NaLi triplet ground state
Authors: Timur M. Rvachov, Hyungmok Son, Juliana J. Park, Sepehr Ebadi, Martin W. Zwierlein, Wolfgang Kette
Keywords: ultracold molecules, triplet states, photoassociation, molecular spectroscopy
Abstract: We employ two-photon spectroscopy to study the vibrational states of the triplet ground state potential (a3?+) of the 23Na6Li molecule. Pairs of Na and Li atoms in an ultracold mixture are photoassociated into an excited triplet molecular state, which in turn is coupled to vibrational states of the triplet ground potential. Vibrational state binding energies, line strengths, and potential fitting parameters for the triplet ground a3?+ potential are reported. We also observe rotational splitting in the lowest vibrational state.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.121.213201
Volume: 121 Issue: 21 First Page #:
Date Submitted: 2/6/19 12:00AM Date Published: 11/1/18 12:00AM
Publication Location:
Article Title: 3D Magneto-Optical Trap of Yttrium Monoxide
Authors: Alejandra L. Collopy, Shiqian Ding, Yewei Wu, Ian A. Finneran, Loïc Anderegg, Benjamin L. Augenbrau
Keywords: magneto-optical trap, diatomic molecules, ultracold molecules
Abstract: We report three-dimensional trapping of an oxide molecule (YO), using a radio-frequency magneto-optical trap (MOT). The total number of molecules trapped is ?1.5×10^4, with a temperature of 4.1(5) mK. This diversifies the frontier of molecules that are laser coolable and paves the way for the second-stage narrow-line cooling in this molecule to the microkelvin regime. Futhermore, the new challenges of creating a 3D MOT of YO resolved here indicate that MOTs of more complex nonlinear molecules should be feasible as well.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review A
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevA.96.063420
Volume: 96 Issue: 6 First Page #:
Date Submitted: 2/6/19 12:00AM Date Published: 12/1/17 5:00AM
Publication Location:
Article Title: Controlling spin flips of molecules in an electromagnetic trap
Authors: David Reens, Hao Wu, Tim Langen, Jun Ye
Keywords: Cold and ultracold molecules, Fine & hyperfine structure, Molecular spectra, Molecule trapping & guiding, Stark effect, Zeeman effect
Abstract: Doubly dipolar molecules exhibit complex internal spin dynamics when electric and magnetic fields are both applied. Near magnetic trap minima, these spin dynamics lead to enhancements in Majorana spin-flip transitions by many orders of magnitude relative to atoms and are thus an important obstacle for progress in molecule trapping and cooling. We conclusively demonstrate and address this with OH molecules in a trap geometry where spin-flip losses can be tuned from over 200 s?1 to below our 2 s?1 vacuum-limited loss rate with only a simple external bias coil and with minimal impact on trap depth and gradient.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Chemistry Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1039/C8CP00962G
Volume: 20 Issue: 17 First Page #: 11615
Date Submitted: 2/6/19 12:00AM Date Published:
Publication Location:
Article Title: Enhancing radical molecular beams by skimmer cooling
Authors: Hao Wu, David Reens, Tim Langen, Yuval Shagam, Daniela Fontecha, Jun Ye
Keywords: free radical, molecular beam, supersonic beam
Abstract: A high-intensity supersonic beam source has been a key component in studies of molecular collisions, molecule–surface interaction, chemical reactions, and precision spectroscopy. However, the molecular density available for experiments in a downstream science chamber is limited by skimmer clogging, which constrains the separation between a valve and a skimmer to at least several hundred nozzle diameters. A recent experiment (Sci. Adv., 2017, 3, e1602258) has introduced a new strategy to address this challenge: when a skimmer is cooled to a temperature below the freezing point of the carrier gas, skimmer clogging can be effectively suppressed. We go beyond this proof-of-principle work in several key ways. Firstly, we apply the skimmer cooling approach to discharge-produced radical and metastable beams entrained in a carrier gas. We also identify two different processes for skimmer clogging mitigation—shockwave suppression at temperatures around the carrier gas freezing point and diffusi
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Nature Physics

Publication Identifier Type: DOI Publication Identifier: 10.1038/s41567-018-0191-z

Volume: 14 Issue: 9 First Page #: 890

Date Submitted: 2/6/19 12:00AM Date Published: 6/1/18 4:00AM

Publication Location:

Article Title: Laser cooling of optically trapped molecules

Authors: Loïc Anderegg, Benjamin L. Augenbraun, Yicheng Bao, Sean Burchesky, Lawrence W. Cheuk, Wolfgan

Keywords: ultracold molecules, optical trapping, laser cooling

Abstract: Ultracold molecules are ideal platforms for many important applications, ranging from quantum simulation and quantum information processing to precision tests of fundamental physics.. Producing trapped, dense samples of ultracold molecules is a challenging task. One promising approach is direct laser cooling, which can be applied to several classes of molecules not easily assembled from ultracold atoms. Here, we report the production of trapped samples of laser-cooled CaF molecules with densities of 8?×?10^7 cm?3 and at phase-space densities of 2?×?10^?9, 35 times higher than for sub-Doppler-cooled samples in free space. These advances are made possible by efficient laser cooling of optically trapped molecules to well below the Doppler limit, a key step towards many future applications. These range from ultracold chemistry to quantum simulation, where conservative trapping of cold and dense samples is desirable. In addition, the ability to cool optically tra

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Physical Review Letters

Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.121.013202

Volume: 121 Issue: 1 First Page #:

Date Submitted: 2/6/19 12:00AM Date Published: 7/1/18 4:00AM

Publication Location:

Article Title: Magnetic Trapping of an Ultracold Gas of Polar Molecules

Authors: D.?J. McCarron, M.?H. Steinecker, Y. Zhu, D. DeMille

Keywords: ultracold molecules, magnetic trapping,

Abstract: We demonstrate the efficient transfer of molecules from a magneto-optical trap into a conservative magnetic quadrupole trap. Our scheme begins with a blue-detuned optical molasses to cool SrF molecules to ?50 ?K. Next, we optically pump the molecules into a strongly trapped sublevel. This two-step process reliably transfers ?40% of the molecules initially trapped in the magneto-optical trap into a single quantum state in the magnetic trap. Once loaded, the molecule cloud is compressed by increasing the magnetic field gradient. We observe a magnetic trap lifetime of over 1 s. This opens a promising new path to study ultracold molecular collisions, and potentially to produce quantum-degenerate molecular gases via sympathetic cooling with co-trapped atoms.

Distribution Statement: 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: New Journal of Physics
Publication Identifier Type: DOI Publication Identifier: 10.1088/1367-2630/aaba65
Volume: 20 Issue: 4 First Page #: 043031
Date Submitted: 2/6/19 12:00AM Date Published: 4/1/18 4:00AM
Publication Location:
Article Title: An approach to spin-resolved molecular gas microscopy
Authors: Jacob P Covey, Luigi De Marco, Óscar L Acevedo, Ana Maria Rey, Jun Ye
Keywords: ultracold molecules, optical lattice, spin diffusion
Abstract: Ultracold polar molecules are an ideal platform for studying many-body physics with long-range dipolar interactions. Experiments in this field have progressed enormously, and several groups are pursuing advanced apparatus for manipulation of molecules with electric fields as well as single-atom-resolved in situ detection. Such detection has become ubiquitous for atoms in optical lattices and tweezer arrays, but has yet to be demonstrated for ultracold polar molecules. Here we present a proposal for the implementation of site-resolved microscopy for polar molecules, and specifically discuss a technique for spin-resolved molecular detection. We use numerical simulation of spin dynamics of lattice-confined polar molecules to show how such a scheme would be of utility in a spin-diffusion experiment.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review A
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevA.96.042712
Volume: 96 Issue: 4 First Page #:
Date Submitted: 2/6/19 12:00AM Date Published: 10/1/17 4:00AM
Publication Location:
Article Title: No evaporative cooling of nitric oxide in its ground state
Authors: Lucie D. Augustovi?ová, John L. Bohn
Keywords: ultracold molecules, evaporative cooling, nitric oxide
Abstract: Cold collisions of 14N16O molecules in the 2?1/2 ground state, subject to electric and magnetic fields, are investigated. It is found that elastic collision rates significantly exceed state-changing inelastic rates only at temperatures above 0.5 K at laboratory-strength fields. It is found, however, that in very large fields, >10^4 V/cm, inelastic rates can be somewhat suppressed. Magnetic fields have a negligible influence on scattering for this nearly nonmagnetic state.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review A
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevA.97.062703
Volume: 97 Issue: 6 First Page #:
Date Submitted: 2/7/19 12:00AM Date Published: 6/1/18 4:00AM
Publication Location:
Article Title: NO evaporative cooling in the
Authors: Lucie D. Augustovicová, John L. Bohn
Keywords: cold and ultracold molecules, evaporative cooling, nictric oxide
Abstract: The scattering at ultralow temperatures of fermionic ^14N^16O molecules in the metastable ^2?_3/2 is considered, under the influence of parallel electric and magnetic fields. It is found that a magnetic field of several thousand Gauss can enhance the ratio of elastic-to-inelastic collision rates. The magnetic field can therefore assist the electric field in increasing this ratio. Evaporative cooling of NO is feasible only in the presence of combined magnetic and electric fields and for temperatures above about 70 mK.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review A
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevA.96.032718
Volume: 96 Issue: 3 First Page #:
Date Submitted: 2/7/19 12:00AM Date Published: 9/1/17 4:00AM
Publication Location:
Article Title: Adimensional theory of shielding in ultracold collisions of dipolar rotors
Authors: Maykel L. González-Martínez, John L. Bohn, Goulven Quéméner
Keywords: ultracold molecules, ultracold collisions, dipolar molecules, Stark effect
Abstract: We investigate the electric field shielding of ultracold collisions of dipolar rotors, initially in their first rotational excited state, using an adimensional approach. We establish a map of good and bad candidates for efficient evaporative cooling based on this shielding mechanism, by presenting the ratio of elastic over quenching processes as a function of a rescaled rotational constant \tilde{B}=B/s_E_3 and a rescaled electric field \tilde{F} =dF/B. B,d,F, and s_E_3 are respectively the rotational constant, the full electric dipole moment of the molecules, the applied electric field, and a characteristic dipole-dipole energy. We identify two groups of bi-alkali-metal dipolar molecules. The first group, including RbCs, NaK, KCs, LiK, NaRb, LiRb, NaCs, and LiCs, is favorable with a ratio over 1000 at collision energies equal to (or even higher than) their characteristic dipolar energy. The second group, including LiNa and KRb, is not favorable. More generally, for molecules we
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review A
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevA.98.023419
Volume: 98 Issue: 2 First Page #:
Date Submitted: 2/7/19 12:00AM Date Published: 8/1/18 4:00AM
Publication Location:
Article Title: Manifestation of quantum chaos in Fano-Feshbach resonances
Authors: Lucie D. Augustovi?ová, John L. Bohn
Keywords: quantum chaos; ultacold collisions; Feshbach resonance
Abstract: A model is presented that mimics the nearest-neighbor-spacing (NNS) distribution of chaotic molecules such as Dy_2 and Er_2 just below their dissociation threshold. In this model the degree of chaos is controlled by choosing suitable Hamiltonian matrices from random ensembles. It is found that, in versions of the model that are not completely chaotic, the NNS of observable Fano-Feshbach resonances exhibits greater level repulsion, hence more chaos, than the corresponding NNS of a typical energy spectrum of the molecule at a fixed magnetic field.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.chemphys.2018.02.017
Volume: 514 Issue: First Page #: 150
Date Submitted: 2/8/19 12:00AM Date Published: 10/1/18 4:00AM
Publication Location:
Article Title: Supersonic beams of mixed gases: A method for studying cold collisions
Authors: William E. Perreault, Nandini Mukherjee, Richard N. Zare
Keywords: supererereresonic molecular beams, cold molecular collisions, stererodynamics
Abstract: We show that collisions in a single supersonic molecular beam reach characteristic temperatures in the range of a few Kelvin. Experiments have been carried out for mixtures of H2 and HD as well as HD and D2 in a pulsed supersonic expansion. From the measured time-of-flight spectrum, we find that the high velocity edge of the distribution for both species is nearly coincident, but the average speed of the heavier species is slightly greater than the lighter one. By working in the few Kelvin regime, this relatively simple technique reduces the number of partial waves in the collision process, which allows the observation of collision resonances. Additionally, copropagation of scattering partners in a single molecular beam precisely defines the direction of their relative velocity vector, which is essential for the study of stereodynamics.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nature Chemistry
Publication Identifier Type: DOI Publication Identifier: 10.1038/s41557-018-0028-5
Volume: 10 Issue: 5 First Page #: 561
Date Submitted: 2/8/19 12:00AM Date Published: 4/1/18 4:00AM
Publication Location:
Article Title: Cold quantum-controlled rotationally inelastic scattering of HD with H2 and D2 reveals collisional partner reorientation
Authors: William E. Perreault, Nandini Mukherjee, Richard N. Zare
Keywords: cold molecular collisions, rortationally ineleastic scattereirng, hydrogen molecules
Abstract: Molecular interactions are best probed by scattering experiments. Interpretation of these studies has been limited by lack of control over the quantum states of the incoming collision partners. We report here the rotationally inelastic collisions of quantum-state prepared deuterium hydride (HD) with H2 and D2 using a method that provides an improved control over the input states. HD was coexpanded with its partner in a single supersonic beam, which reduced the collision temperature to 0–5?K, and thereby restricted the involved incoming partial waves to s and p. By preparing HD with its bond axis preferentially aligned parallel and perpendicular to the relative velocity of the colliding partners, we observed that the rotational relaxation of HD depends strongly on the initial bond-axis orientation. We developed a partial-wave analysis that conclusively demonstrates that the scattering mechanism involves the exchange of internal angular momentum between the colliding partners. The striki
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Science
Publication Identifier Type: DOI Publication Identifier: 10.1126/science.aao3116
Volume: 358 Issue: 6361 First Page #: 356
Date Submitted: 2/8/19 12:00AM Date Published: 10/1/17 4:00AM
Publication Location:
Article Title: Quantum control of molecular collisions at 1 kelvin
Authors: William E. Perreault, Nandini Mukherjee, Richard N. Zare
Keywords: cold molecular collisions, stereochemeistry, rotationally inelastic collisions, quantum control
Abstract: Measurement of vector correlations in molecular scattering is an indispensable tool for mapping out interaction potentials. In a coexpanded supersonic beam, we have studied the rotationally inelastic process wherein deuterium hydride (HD) (v = 1, j = 2) collides with molecular deuterium (D2) to form HD (v = 1, j = 1), where v and j are the vibrational and rotational quantum numbers, respectively. HD (v = 1, j = 2) was prepared by Stark-induced adiabatic Raman passage, with its bond axis aligned preferentially parallel or perpendicular to the lab-fixed relative velocity. The coexpansion brought the collision temperature down to 1 kelvin, restricting scattering to s and p partial waves. Scattering angular distributions showed a dramatic stereodynamic preference (~3:1) for perpendicular versus parallel alignment. The four-vector correlation measured between the initial and final velocities and the initial and final rotational angular momentum vectors of HD provides insight into the strong
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

DISSERTATIONS:

Publication Type: Thesis or Dissertation
Institution:
Date Received: 30-Aug-2014 Completion Date:
Title: Interacting Quantum Gases of Lithium and Ytterbium
Authors:
Acknowledged Federal Support:

Publication Type: Thesis or Dissertation
Institution:
Date Received: 30-Aug-2014 Completion Date:
Title: Experiments in the Ultracold Lithium - Ytterbium System
Authors:
Acknowledged Federal Support:

Publication Type: Thesis or Dissertation
Institution:
Date Received: 30-Aug-2014 Completion Date:
Title: Laser cooling and slowing of a diatomic molecule
Authors:
Acknowledged Federal Support:

Publication Type: Thesis or Dissertation
Institution: University of Washington
Date Received: 16-Oct-2017 Completion Date: 10/15/17 6:28PM
Title: Ytterbium and Lithium Quantum Gases: Heteronuclear Molecules and Bose-Fermi Superfluid Mixtures
Authors: Richard Roy
Acknowledged Federal Support: **N**

RPPR Final Report
as of 24-Apr-2019

Publication Type: Thesis or Dissertation
Institution: Massachusetts Institute of Technology
Date Received: 16-Oct-2017 Completion Date: 6/1/16 4:00AM
Title: An Ultracold Gas of Dipolar Fermionic 23Na40K Molecules
Authors: Jee Woo Park
Acknowledged Federal Support: **Y**

We discuss below progress in each of the three main thrusts of our research effort. In addition to these primary lines of progress, team members published severeral reviews of the field in prominent journals. These included a Spotlight article "Ultracold molecules and the dawn of cold controlled chemistry" in J. Chem. Phys, and two invited reviews: "Cold Molecules: Progress in Quantum Engineering of Chemistry and Quantum Matter," in Science, and "New frontiers for quantum gases of polar molecules," in Nature Physics. Many of our team's results were published in a Special Issue of the New Journal of Physics, on "New Frontiers of Cold Molecules Research", edited by co-PIs DeMille and Ye (together with two collaborators from outside the MURI).

1. Chemistry in the quantum degenerate regime:

Our team studied and/or prepared several new systems of molecules in the quantum degenerate regime, with work including both experiment and theory. Some highlights of our progress in this area include:

- Experimental production of an optically trapped gas of fermionic ^{23}Na^{40}K molecules in their absolute ground state (rovibronic and hyperfine), at temperatures of a few hundred nanoKelvin. NaK is the first molecular species available in this temperature regime for which the ground state is not chemically reactive with other molecules of the same state and species. In addition, its fermionic nature prohibits two-body collisions of any type at these low temperatures. This will make NaK uniquely suitable for studying reaction dynamics in future studies, since reactions can be initiated at a known time using lasers to vibrationally excite the molecules. Moreover, NaK possesses a large induced dipole moment of up to 2.7 Debye, making it an also ideal candidate for future work in quantum information and quantum simulation based on dipole-dipole interactions between molecules.

The hyperfine spin-polarized, nearly quantum degenerate gas of several thousand NaK molecules displays a lifetime longer than 2.5 s, highlighting NaK's stability against two-body chemical reactions. Homogeneous electric fields have been applied to induce a dipole moment of up to 0.8 Debye, the largest in any ultracold gas to date, highlighting the potential for quantum control of strong dipole-dipole interactions between molecules.

We demonstrated significant quantum-level control over the trapped NaK molecules. For example, rapid coherent Rabi oscillations were observed between the ground and excited rotational states as well as between nuclear hyperfine states. We observed a nuclear spin coherence time on the order of one second in this bulk molecular gas, which signals a new regime of quantum control over the internal degrees of freedom of molecules. In work yet to be published, we are now completing a study of the stability of the NaK molecular gas in the presence of microwave-induced dipolar interactions.

To produce ultracold NaK, we start with weakly bound Feshbach molecules, bound by only 4 microK (equivalent to 330 pico-eV). A coherent two-photon (STIRAP) process subsequently transfers molecules into the absolute rovibrational and hyperfine ground state, where they are bound by 0.65 eV. Finding a successful pathway towards the creation of ultracold ground state molecules required extensive photoassociation spectroscopy on Na-K mixtures and one and two-photon spectroscopy on Feshbach molecules. This provided crucial spectroscopic information on the previously unexplored molecular states of ^{23}Na^{40}K. Based on these data, we identified electronically excited intermediate states that enabled efficient STIRAP transfer to the ground state. Using this knowledge on intermediate states, we then performed two-photon spectroscopy to measure the binding energy of vibrational states close to the dissociation limit of both the $^1\Sigma$ and $^3\Sigma$ NaK ground state potentials. We first identified many high-lying vibrational states of the NaK triplet potential, then the triplet ground state, and ultimately spectroscopically located the absolute rovibrational ground state in the singlet potential. The binding energy was measured with ~10 nano-eV accuracy.

Since the particular Feshbach molecules are mostly triplet in character, while the ground state is singlet, the excited state used for two-photon transfer had to be a sufficiently mixed state of both singlet and triplet character. Two possible choices of excited states with anomalously strong singlet-triplet mixing were identified in our spectroscopic data, originating from an accidental near-perfect degeneracy between bare singlet and triplet states. These excited states were used to find and ultimately populate the absolute rovibrational ground state of NaK.

We note that our results demonstrated the ability to perform coherent two-photon spectroscopy with two lasers spaced apart by 156 THz, bridging an energy gap of 7500 Kelvin from Feshbach molecules to absolute ground state molecules. In this coherent two-photon process, two molecular states whose size differs by a factor of about 300--from several 1000 a_0 to 3.5 a_0--were coherently coupled. These results improved our knowledge of the long-range part of the ground state potentials (C6, C8, C10 coefficients), which are needed to understand molecular binding energies and atomic collision properties.

In order to perform this work, On the hardware side, we successfully developed a diode laser system with fast feedback electronics that allows enabled phase-locking of two independent lasers. This is important because efficient STIRAP transfer between molecular vibrational states requires a phase-coherent laser system. For a typical 10 us STIRAP sequence, the relative linewidth of the two lasers must be ~10 kHz or better; we achieved a relative linewidth of 100 Hz or better. For phase-locked lasers with a frequency difference of up to 10 GHz, we observed a coherent beat signal that is 50dB above noise level, more than 10dB better than typically reported in literature.

- Experimental production of a long-lived, optically trapped gas of fermionic ^{7}Li^{23}Na molecules in the absolute ground state of their metastable triplet state. This molecular species is the first in the ultracold regime that features a magnetic dipole moment as well as an electric dipole moment. This allows for more handles for quantum coherent manipulation than singlet molecules. We have demonstrated that the triplet ground-state NaLi molecules have a long lifetime of >4 seconds, approaching the universal rate limit for inelastic collisions. We measured the hyperfine structure in the NaLi triplet molecule using electron spin resonance spectroscopy, a technique only possible in molecules with non-zero magnetic moment.

Much as for NaK, formation of LiNa molecules required extensive study of the NaLi triplet state potentials, performed using one- and two-photoassociation spectroscopy. For this initial stage of the work, a mixture of Na and Li atoms was evaporatively cooled in a magnetic trap to microkelvin temperatures. Photoassociation to the electronically excited c $^3\Sigma$ state was induced by illuminating the sample with tunable diode lasers and recording trap loss of both atomic species. Since no prior spectroscopy of the triplet states of NaLi had been done before, we had to start from the most weakly bound states in the c $^3\Sigma$ potential, which can be excited at a frequency close to the atomic resonance of lithium. Using the identified lines to improve the predictions for lower-lying states, we worked our way down to nearly the bottom of the ab initio-predicted well depth. Our data yielded accurate measurements of C_6 and C_8 coefficients and predictions for even lower states. Nearly all excited vibrational states were found to ~MHz resolution, and measurements of the photoassociation loss rates to these vibrational levels showed excellent agreement with theoretical Frank-Condon calculations.

Using an intermediate state from this now well-determined excited molecular potential, we next performed two-photon dark-resonance spectroscopy to find all of the vibrational levels in the NaLi triplet ground potential. Based on this data, we formed NaLi triplet ground state molecules via two-photon stimulated Raman adiabatic passage (STIRAP). This work involved close collaboration with the NaK effort for developing the laser technology for the two-photon STIRAP.

In related work, we also studied collisional loss of ultracold ^{6}Li$_2$ molecules. We found that the loss rates can be determined by physics beyond universal long-range van der Waals interactions. For ^{6}Li$_2$ in its highest vibrationally excited state, Li$_2$+Li$_2$ and Li$_2$+Na collisions are well-described by a simple, universal quantum Langevin model. In contrast, Li$_2$ + Li collision rates are found to be exceptionally small due to the low density of states for the outgoing channels of such light collision partners. This was the first clear observation of non-universal behavior in collisions of ultracold molecules.

- Continued experimental and theoretical study and improved quantum control of optically-trapped, ultracold KRb molecules. On the experimental side, team members at JILA (in collaboration with the group of D. Jin) constructed and began experiments using a new, second generation apparatus for producing ultracold gases of KRb, following their ground-breaking work prior to the MURI. In this new apparatus, high resolution optical imaging and precise control of high electric fields for tuning of molecular interactions were implemented. We produced a deeply degenerate quantum gas of KRb molecules loaded in a 3D optical lattice, with an entropy per molecule reaching 2.6 k_B (where ~1 k_B corresponds to the threshold for Fermi degeneracy). This system was used to study Bose-Fermi mixture doublon dynamics in a 3-D optical lattice.

Prior to this, we reported observation of spin-exchange interactions driven by electric dipole-dipole interactions between molecules at distance sites in an optical lattice. This work represents an important benchmark in the control over very long-distance interactions between molecules in the ultracold regime.

We also developed and experimentally verified a theoretical model to explain the observed suppression of the rate of chemical reactions between KRb molecules, when the molecules are held in an optical lattice that should be weak enough for them to move rapidly between sites and hence quickly react. We showed that the reaction-rate suppression is a consequence of the combined effects of lattice confinement and the continuous quantum Zeno effect.

Theorists in the team performed numerically-exact quantum mechanical calculations for the $K+KRb \rightarrow K_2+Rb$ reaction in the ultracold regime. Here, we found that the role of the non-additive three-body contribution to the potential and to the total reactive scattering of KRbK is small. We take this as evidence for the validity of universal models when applied to heavy alkali atom + diatom reactions. We obtained a total rate coefficient in good agreement with the experimental results. We also calculated rovibrationally resolved reaction rates for this system. Thought the total rate coefficient agrees with predictions from the universal model, the short range dynamics is chaotic in nature, leading to a Poisson distribution of the rotational-product rate coefficients.

We also calculated dynamic polarizabilities of the rotational hyperfine states of ultracold dipolar molecules in their ground electro-vibrational level when a magnetic field, a strong static electric field, and a trapping laser field are simultaneously applied. The electric field was found to be especially useful for creating hyperfine-state-insensitive trapping conditions, i.e. conditions where states of the interest experience identical trapping potentials independent of fluctuations of the laser intensity. This should enable precise control over nuclear spin and hyperfine degrees of freedom, similar to that demonstrated in NaK, but now in KRb and other bi-alkali molecules.

- Experimental and theoretical progress toward production of ultracold LiYb molecules. LiYb, like LiNa, has both magnetic and electric dipole moments; here, however, this property is found in the absolute ground state of the molecule rather than in a metastable triplet state as for LiNa. Hence it is a true free radical, with potential for further forms of quantum control. Producing LiYb is quite different from producing bialkali species such as NaK, LiNa, and KRb, since in those cases the method relies heavily on the existence of Fano-Feshbach resonances that are not present in a similar form in $^2\Sigma$ state molecules such as LiYb. Moreover, there was almost no information about molecular potentials and scattering properties in LiYb prior to our work.

Hence, our efforts to produce LiYb involved a particularly tight linkage between experiment and theory.

Although in this system we did not yet succeed in producing ground state LiYb molecules, we have completed nearly all of the experimental steps and gained nearly all the theoretical knowledge needed to do so, in the very near future. In particular, we have

--realized a Bose-Fermi double superfluid composed of Li and Yb atoms

--implemented one and two-photon photoassociation spectroscopies in an optical dipole trap, and interpreted these data using our theoretical study of interaction potentials and dispersion coefficients between Yb and Li atoms in several different electronic states. With the combined experimental and theoretical data, we identified and precisely located the energies of several LiYb rovibrational levels in both excited and ground electronic states.

--analyzed the dependence of vibrationally averaged dipole moments between the initial scattering wave function and excited rovibrational states on vibrational level, v, with a combination of experimental and theoretical data. This made it possible to estimate the Rabi frequencies for free-bound and bound-bound transitions (checked experimentally via atom loss and Autler-Townes spectroscopy, respectively).

--Based on this analysis, we identified a particular, optimized pair of excited and ground states where implementing STIRAP for efficient transfer from free states to bound states in the ground electronic potential should be feasible

--Finally, we recently observed atom-molecule dark states in the LiYb system, a critical precursor for ground-state molecule formation.

In one spin-off from this main line of work, the LiYb effort also resulted in development of a general and readily-adoptable technique using time-averaged optical potentials to improve the efficiency and speed of quantum degenerate gas production. Notably, this made it possible to produce Bose-Einstein condensates (BEC) with production cycle times as low as 1.6 seconds, the fastest to-date in optical traps. Using this method with the dual-species Yb-Li system resulted in an order-of-magnitude improvement in the particle numbers at quantum degeneracy. This new trap manipulation method is applicable towards improving the efficiency of molecule formation, by improving the spatial overlap of the constituent atoms, prior to free-bound coupling. This work also identified the previously unknown sign of the ground state scattering length a(Li-Yb), which provides important input for calculations of the Li-Yb ground state potential.

In another spin-off direction, we observed magnetic field dependent processes in collisions between fermionic ^{6}Li atoms and bosonic metastable ^{174}Yb*($^3P_2$) atoms. The behavior was linked, via extensive theoretical analysis using coupled-channels calculations, to novel types of magnetic Feshbach resonances in this system that arise from the combined effect of anisotropicmolecular and atomic–hyperfine interactions. This made it possible to theoretically evaluate the feasibility to form magnetically-tunable Feshbach LiYb molecules in metastable electronic states, and to understand elastic and inelastic rates in collisions between ultracold Li and Yb* atoms. In addition, dynamic polarizabilities of the various Yb metastable states were determined with good agreement between experiment and theory.

Finally, motivated by this progress towards forming ultracold LiYb molecules, theorists in our team calculated quantum dynamics of the LiYb + Li → Li_2 + Yb reaction. This yielded predictions for state-to-state rate coefficients in the 1 μK-1 K range. To complete these calculations, we constructed the long and short-range potential surface of the 3-body collisional LiLiYb complex; in parallel, we applied a simplified Statistical QM method as well as a Universal QDT to compare with the exact results. Our calculations yielded rate coefficients that are fully resolved with respect to vibrational and rotational quantum numbers of the product Li_2 molecule. The overall reaction rate coefficients from our detailed calculations were in reasonable agreement with predictions based on the universal model and a quantum statistical model. We also investigated sensitivity of the rate coefficients to three-body forces in the interaction potential, by comparing results obtained using with and without this contribution to the potential. We found that neglect of the three-body term leads to a factor of two discrepancy in the zero-temperature rate coefficients, and marked changes in the vibrational and rotational distributions of the product Li_2 molecule. Thus, we conclude that while simplified schemes based on universal models may be employed to evaluate the overall rate coefficients for ultracold reactions, a rigorous quantum mechanical treatment using an accurate interaction potential is needed for evaluating product distribution.

- Experimental investigation of a simplified approach to creating quantum-degenerate gases of bi-alkali molecules. Here, we studied the possibility to replace the complex Feshbach resonance + STIRAP procedure used in previously successful molecular quantum gas experiments. The goal was to use simple one-photon photoassociation to produce absolute ground state molecules, followed by inelastic collisional "scrubbing" of unwanted excited states that are inadvertently populated. These studies were performed using RbCs molecules.

We experimentally studied a variety of novel photoassociation pathways, based on intermediate-range excited states at higher energies than had been explored previously. We demonstrated several pathways that produced absolute ground-state molecules with efficiency as high as ~10%, due to strong local nonadiabatic couplings between singlet and triplet excited-state potentials. We also characterized the distribution of unwanted rovibrational states produced in this process.

We also studied collisional loss of ground-state RbCs molecules when trapped alone, or co-trapped with Rb or Cs atoms. Our observations appeared to show no difference in collisional losses when trapped with Rb (which can react with RbCs) or Cs (which cannot). This was a deeply surprising result, which persisted even after numerous systematic error checks. This led us to suspect that RbCs+Cs ultracold collisions form long-lived complexes that lead to the appearance of molecule loss in the system. However, the existence of a few additional possible explanations left us without sufficient confidence to publish this result. (We heard, around the same time, of similar observations in several other bialkali systems from groups outside the MURI team, but these groups also did not feel confident enough to publish their results.) In the past year, finally another group outside the MURI did publish data showing similar loss behavior in NaRb + Na or Rb collisions, with very careful control of possible alternate loss mechanisms. Hence, we have concluded that our unpublished results were likely correct after all—and hence that the notion of collisional "scrubbing" of vibronically excited states is not a viable approach to creating a gas of pure ground-state ultracold molecules.

As part of this work, we also observed and characterized in detail dozens of new rovibronically-excited states in RbCs. This included assignment of electronic state quantum numbers, rotational constants, and hyperfine constants.

- We also explored a wide variety of theoretical issues related to new methods for quantum-level control of ultracold molecular systems and novel features in collisional and chemical reaction dynamics that appear at ultracold temperatures. For example:

  --We examined the connection between symmetry and geometric phase effects in H+HD and D+HD reactions at ultracold temperatures.

  --We explored long-lived resonances and signatures of chaotic dynamics in K_2+Rb collisions.

  --We completed a study with the goal to develop theoretical models of and practical applications for conical intersections with their geometric phases, to ultracold chemical reactions with molecules confined in optical potentials. This work focused on heteronuclear polar molecules that are laser cooled to μK or nK temperatures—primarily ground-state alkali-metal molecules that can collide with each other or with their constituent atoms and undergo chemical reactions. We investigated non-adiabatic nuclear reaction dynamics of intermediate trimer complexes in collisions between ultracold, laser-cooled and trapped heteronuclear molecules. The search for the dynamic signatures of non-adiabatic passage through the conical intersection made it possible to distinguish between relaxation and reaction pathways, and to build a bridge between computational approaches developed within the physical chemistry community and advanced tools for describing ultracold collisions of atoms and molecules used in the atomic physics community.

  -- In work with non-MURI collaborator Dr. Brian Kendrick (LANL), we addressed the important issue of geometric phase effect in chemical reactions. This is a longstanding issue in chemical reaction dynamics. Our work showed that the geometric phase effect becomes important, and a indeed even a controlling factor, in ultracold reactions.

--We studied the thermodynamics of a cold, but not yet quantum degenerate, gas of dipolar particles—the environment of ultracold molecular species at the current state of experimental techniques. We studied rethermalization dynamics in sufficient detail to extract the first scattering length information on a highly polar species, Dy atoms (in collaboration with the group of B. Lev at Stanford).

--In related work, we performed calculations to interpret the landmark experimental results on ultracold collisions of strongly dipolar Er atoms (in the experimental group of F. Ferlaino, Innsbruck). Through a combination of our quantum scattering calculations and our semiclassical analysis, these results demonstrated, for the first time, the occurrence of quantum chaos in ultracold scattering. This observation has the potential to shift the paradigm of cold molecular collision studies, from trying to interpret and catalog every resonance (a nearly impossible task for a chaotic system) to instead viewing spectra of complex scattering partners, and their control, within alternative statistical frameworks.

--In a spin-off project, we probed the basic physics of the "unitary Bose gas," when an atomic BEC is suddenly quenched to a scattering length that is formally infinite. Strikingly, detailed calculations of three-body recombination in this regime supported the experimental finding that this chemical process is surprisingly slow in this unique environment, thus allowing the gas to proceed toward local equilibrium.

2. Improved methods of control in the cold regime

Our team also studied and/or prepared several new systems of molecules in "merely cold" regime, with temperatures in the range of a few Kelvin. Some highlights of our progress in this area include:

- We demonstrated the use of infrared optical frequency comb spectroscopy for real-time monitoring of chemical reaction kinetics. This new method of simultaneously probing population in a wide range of molecular vibrational states has allowed us to gain insights into complex structure and coupling dynamics in large molecules, and even enables detection of transient species during chemical reactions. We demonstrated the method by measuring the evolution of population of reactants and products, as well as of the transient intermediary species DOCO, during the reaction of OD with CO. In our technique, cooling to cryogenic temperatures via buffer gas cooling is crucial to achieving frequency comb spectra with enough simplicity to interpret the results. This opens a new route to gaining insights into complex structure and coupling dynamics in large molecules and their reaction intermediates.

- Experimental development of a method to efficiently prepare H_2, HD, and D_2 molecules in single, selected rovibrationally-excited states. Moreover, this technique naturally prepares states with well-defined and controllable alignment of the rotational angular momentum. This work was based on major advances in the technique of Stark-induced adiabatic Raman passage

(SARP), a close relative to STIRAP that is effective in systems where electronic resonances lie far higher in energy than can be reached with high-power tunable lasers. This capability of preparing selected, excited vibrational levels of molecules with tightly-bound shells opens new opportunities for studying low temperature collisions, where vibrational excitation often plays a crucial role in overcoming the barrier to a reaction.

Our team completed several distinct demonstrations of the capabilities of the SARP technique, using hydrogen molecules in a supersonic beam with temperatures of ~1 K. This included efficient population of states such as:

--HD in the vibrationally excited state (v=4, j=0), resulting in a large population ($>10^{10}$ molecules per laser pulse)

-- H_2 in vibrationally excited state (v=1, J=0), with almost complete (97%) transfer from the (v=0, J=0) ground state.

--H_2 in the vibrationally and rotationally excited state (v=1, J=1) (in all M-sublevels)

--axially polarized para-H_2 molecules in the rovibrationally excited (v=1, J=2, M=0) state

--rovibrationally excited (v=1, J=2) right handed (M = +2) or left handed (M = -2) spinning H_2 molecules

--partially polarized ortho-H_2 molecules in the rovibrational excited (v=1, J=3) state

--an aligned state of H_2 with the form $|v=1,J=2,M=-2\rangle - |v=1,J=2,M=+2\rangle$, with over 60% efficiency of excitation from the ground state. For this case of a coherent superposition state, the degree of phase coherence of the superposition was measured using polarized probe laser pulses.

Our results establish SARP as a robust technique applicable to many other molecular species. Preparing molecules in aligned states of angular momentum (a superposition of M-states) provides the unique opportunity to break the cylindrical symmetry normally observed in bimolecular scattering.

- Demonstration of coherent control of cold collision dynamics. We carried out an inelastic scattering experiment using SARP prepared HD molecules scattering on H_2. An important initial step in this work was the realization that, by coexpanding two molecular species in a single supersonic beam, it is possible to bring down the collision temperature to near 1 K where only a few partial waves participate in the collision, making quantum effects readily observable.

Precise stereodynamic control was achieved by selecting orientation-specific (M) states within the rovibrational eigenstate (v=1, j=2) by controlling the polarization direction of the SARP laser fields. This is the first demonstration of a low-energy collision near 1 K with vibrationally and rotationally excited quantum state with a precision of a single angular momentum orientation (M) state. By fitting the angular distribution using partial wave analysis, we were able to measure the four-vector correlation, namely, k, j, k′, j′, where k and k′ are the initial and final velocities in the center of mass frame and j and j′ are the initial and final rotational angular momenta of the hydrogen molecule.

Theorists in our team carried out explicit calculations of quantum dynamics and vector correlations in collisions of rotationally and vibrationally excited HD prepared by the SARP method with H_2. We provided a complete ab initio description of the experiment and attributed keys features of the experimentally observed differential cross sections to a partial wave resonance near 1 K. This provides clear evidence of coherent control over a molecular collision at the quantum level.

- To obtain high resolution velocity map imaging of the angular distribution of the state prepared molecules in reactive scattering, MURI funding was partially utilized to fabricate a high vacuum molecular beam reaction chamber with a time of flight (TOF) spectrometer. We have recently calibrated the spectrometer and measured the recoil of the photoelectron ejected during multiphoton ionization of state-prepared H_2. The half-collision process of photoionization from a resonantly excited rovibrational M-state will allow us to observe the dependence of the photoionization process, which has not been observed before.

- To prepare large ensembles of molecules in higher vibrationally excited quantum states, we developed a theory for how to utilize SARP to accomplish ladder excitation through vibrational levels. We have theoretically and numerically showed that SARP ladder excitation can transfer the complete population of H2 from (v=0) ground level to (v=14), the highest vibrational level within the ground electronic state.

Multi-color SARP's ability to operate in a ladder-like fashion could provide a unique way to achieve coherent dissociation, creating pairs of entangled atoms with high density and near-zero relative velocity.

- We developed a new theoretical approach to the study of cold and ultracold collisions, using multichannel quantum defect theory (MQDT)-based methods. Specifically, we developed a method that combines standard quantum Close Coupling (CC) calculations with Multichannel Quantum Defect Theory (MQDT) methods, in order to calculate molecular reactive and inelastic scattering rates. In prior implementations of the MQDT formalism for ultracold reactions, the short-range dynamics was either treated approximately or entirely avoided by placing absorbing potentials in the strong interaction region, leading to significant errors in calculated rates. In our approach, the short-range dynamics is explicitly treated using CC methods, while MQDT is used to treat the computationally intensive long-range regime. We successfully applied this method to benchmark systems such as quasi-resonant scattering of cold H_2 molecules and to state-selective reactive scattering of $D+H_2/H+D_2$. We also implemented the approach for the benchmark $F+H_2$ reaction.

Our method produced quantitatively accurate results, while proving both conceptually transparent and computationally far less burdensome than conventional methods based entirely on the CC approach. These advances open the door for applications to more complex but more experimentally realizable species in the near future. Of note is the well-known ease with which QDT methods describe the influence of magnetic fields, implying that new pathways for controlling chemical reactions at ultralow temperature can now be explored in detail.

- We used standard methods to theoretically investigate $O(^1D)+H^2$ and $O(^1D)+D^2$ reactions at ultracold temperatures and explored their sensitivity to vibrational excitation of the reactant molecules. We also explored the effect of vibrational excitation of the OH molecule in $O+OH \rightarrow H+O_2$ reaction.

3. Extending the species available in the ultracold

The third major thrust in our team's research was the development of new methods to produce ultracold molecular gases with species very different from those that can be assembled from ultracold atoms (as in thrust number 1). Some highlights of our progress in this area include:

- Major advances in direct laser cooling and trapping of diatomic molecules. As this grant began, laser cooling had been demonstrated on only one species of molecule (SrF), and laser trapping had not been achieved. Support from this MURI grant has led to a dramatic transformation: cooling and trapping methods closely analogous to those used with atoms for nearly 40 years are now, more and more, routinely available for use with molecules. In particular, three distinct groups in our team have now demonstrated both laser cooling and magneto-optical trapping (MOT) of three different molecular species: SrF, CaF, and YO. The MOT is *the* workhorse technique for experiments with ultracold atomic gases, since it simultaneously accumulates, cools, and traps the particles. Learning to make MOTs for molecules is opening the door to a wide host of studies of chemical and collisional dynamics in the ultracold regime. These molecular MOTs have similar properties to atomic MOTs, now routinely producing molecular gases with $\sim 10^4$-10^5 molecules in a volume of ~ 1 mm^3, at temperatures in the range 300-3000 μK and trapped for times of ~1 second.

Making molecular MOTs viable required significant development of experimental methods, beyond those typical for atoms. For example: in order the load the MOT, it is necessary to deliver large numbers of sufficiently slow molecules to the trapping region, and this proved to be a key difficulty in creating a molecular MOT. All three groups in our MURI team used cryogenic buffer gas-cooled molecular beam sources, but the three groups explored a variety of schemes for molecule slowing. In particular, the Harvard and JILA groups worked extensively to use two-stage cryogenic beam sources as a way to create initially slower beams, then used these sources in conjunction with the white-light slowing method developed by the Yale group to load their molecular MOTs with improved efficiency. As another example, all three groups developed various techniques to mitigate the effect of optical pumping into various types of dark states, which can occur easily in molecules due to decay into various undesired electronic, vibrational, rotational, and or spin-orientation states. These techniques included radiofrequency (RF) synchronous switching of magnetic field gradients and polarizations in the MOT, and application of pulsed microwave electric fields. The three groups collaborated to design the required high-Q, low-inductance, in-vacuum magnetic field coils needed for the RF MOT, which has now become the standard approach to making a molecular MOT. In paralle, we explored different techniques for transverse cooling and/or compression of the molecular beam, to improve the efficiency of loading from the beam into the MOT.

In the end, our MURI team's work has resulted in an increasingly standardized set of proven techniques for laser cooling and trapping of molecules, which are now also being implemented in many groups worldwide.

Once MOT operation became routine, we went on to demonstrate sub-Doppler cooling of CaF and SrF molecules after their release from a MOT, reaching temperatures in the range 5-50 μK. This included demonstration of a dark-state enhanced cooling technique, similar to one whose mechanism was only recently understood with atoms, to reach the lowest temperatures.

We went on to demonstrate efficient transfer of these ultracold molecules into conservative traps, including both a magnetic trap (for SrF) and an optical dipole trap (for CaF). These traps are similar to those commonly used for further cooling of ultracold atoms from MOTs, using collision-based methods such as evaporative cooling and/or sympathetic cooling.

Hence, three groups within our team are now poised to attempt further cooling of conservatively-trapped molecules in the near future. For example, we have begun constructing a laser system to co-trap Rb atoms with SrF molecules in a magnetic trap. This will enable us to study the feasibility of sympathetically cooling the molecules as a pathway to achieve vastly lower temperatures and higher densities.

- Work on cooling and diagnosing properties of trapped OH molecules, delivered from a Stark-slowed supersonic beam, progressed significantly. After initial observations of evaporative cooling, we experimentally and theoretically characterized an unanticipated spin flip loss in the previously-used permanent magnetic trap, and designed and implemented a new electric+magnetic trapping geometry to remove this now-understoood loss mechanism. We implemented a new molecular beam valve and skimmer system that delivers significant improvement in molecular throughput, and a new Stark decelerator is under construction to load more OH molecules into the trap.

We demonstrated, theoretically, a new concept that dramatically expands the class of diatomic molecules that are expected to be amenable to cooling to ultracold temperatures via evaporative cooling. This concept is related to our earlier work showing that OH molecules can, when prepared in certain rotational sublevels and subject to a strong electric field, exhibit pure long-range repulsive interactions that suppress inelastic collision cross-sections while enhancing the elastic collisions needed for evaporative cooling. In the new work, we developed a universal scaling theory of collision physics for evaporative cooling, finding that many molecular species in both $^2\Sigma$ and $^1\Sigma$ electronic states—including species that are being directly laser cooled such as SrF, CaF, and YO, plus certain alkali dimers explored in this MURI such as NaK, should be amenable to this technique. This approach opens a highly likely pathway of viability for evaporative cooling of many polar molecules, for the first time.

In related work, we studied the potential for evaporative cooling of NO molecules, a species of significant chemical interest. We found that while this is unlikely to be viable for NO in its ground electronic state, evaporative cooling can proceed for NO in its metastable $^2\Pi_{3/2}$ state.

- We studied prospects for applying strong stimulated optical forces to make laser slowing of molecular beams more widely applicable. As part of this study, we theoretically investigated recent claims of laser cooling of atoms in the absence of spontaneous emission. We found that these claims cannot be supported based on current data; however, our work led to understanding of a fundamental upper rlimit on the rate of laser cooling and showed that a particular stimulated force (the bichromatic force) nearly saturates this limit. A paper based on this work is in preparation.

- Though not directly part of work in this MURI, our team's demonstrations of diatomic molecule laser cooling are now rapidly being applied to triatomic and even larger species. Motivated by this development, we theoretically studied the structure of one such triatomic species, SrOH. We determined the potential energy surfaces (PESs) associated with the formation of the SrOH molecule from collisions of ground state $Sr(^1S)+OH(X^2\Pi)$. Our systematic *ab-initio* study showed that very large basis sets and proper electron correlation treatment are needed to obtain converged results. The optimized geometry for the ground SrOH molecule was found to be linear. The dissociation energy D_e was calculated with estimated accuracy ~3%. Our study also indicates a breakdown of the Born-Oppenheimer approximation at conical intersections (Cis) between the two diabatic potential surfaces. One of these CIs is important for the collision between Sr and the OH radical, because its energy is lower than the asymptotic energy of the entrance channel. Finally, we found that the excited $SrOH(A^2\Pi)$ state exhibits the Renner-Teller effect due to bending motion of the molecule, which splits the twofold degeneracy of the $A^2\Pi$ electronic state.