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1. REPORT DATE (DD-MM-YYYY) 21-08-2018	2. REPORT TYPE Final Report	3. DATES COVERED (From - To) 11-Jan-2017 - 31-May-2018
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4. TITLE AND SUBTITLE Final Report: Control and Spectroscopy of Single Molecular Ions	5a. CONTRACT NUMBER W911NF-17-1-0071
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER 611102

6. AUTHORS	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Georgia Tech Research Corporation 505 Tenth Street NW Atlanta, GA 30332 -0420	8. PERFORMING ORGANIZATION REPORT NUMBER
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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) 69597-PH.7

12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.
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13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed 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:	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Kenneth Brown
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU	19b. TELEPHONE NUMBER 919-660-1376

RPPR Final Report

as of 19-Mar-2019

Agency Code:

Proposal Number: 69597PH

Agreement Number: W911NF-17-1-0071

INVESTIGATOR(S):

Name: Kenneth Brown
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DUNS Number: 097394084

EIN: 580603146

Report Date: 31-Aug-2018

Date Received: 21-Aug-2018

Final Report for Period Beginning 11-Jan-2017 and Ending 31-May-2018

Title: Control and Spectroscopy of Single Molecular Ions

Begin Performance Period: 11-Jan-2017

End Performance Period: 31-May-2018

Report Term: 0-Other

Submitted By: Kenneth Brown

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

STEM Degrees: 2

STEM Participants: 4

Major Goals: The goals of this project were the continued improvement of molecular spectroscopy techniques using molecular ions embedded in Coulomb crystals of laser-cooled atomic ions. The ultimate goal was to devise methods for achieving molecular spectroscopy with single ions. CaH⁺ used as the primary test ion for developing the molecular spectroscopy techniques.

Accomplishments: Between Jan 11, 2017 and May 31, 2018, we examined the resonance enhanced multi-dissociation spectroscopy of CaH⁺ in Coulomb crystals.

Our initial effort focused on understanding the vibronic transitions of CaH⁺. Our previous work showed that the measured vibronic transitions of the first electronic transition of CaH⁺ disagreed with theory. There were two options: either the theory was off by 50 cm⁻¹ and we did not observe a peak or the theory was off by 687 cm⁻¹. Both results seemed unlikely. To distinguish between the options, we performed vibronic spectroscopy on CaD⁺. The isotopologue should have the same electronic splitting in the Born-Oppenheimer picture and only the vibrational levels should shift. This work confirmed that the initial theory was off by 687 cm⁻¹. Our colleague David Sherrill at Georgia Tech performed a more exact calculation that unfroze core electrons in the Ca atom and used a high-level of correlation up to quadruple excitations in a coupled-cluster model. This reduced the theoretical offset to 300 cm⁻¹. This value is still far from spectroscopic accuracy and points to the continued need for experiments to identify molecular ions in the atmosphere and in outer space. This work was published in J. Chem. Phys. in Dec. 2017.

We then turned our attention to the rovibronic spectroscopy of CaH⁺. First we used pulse shaping to narrow the linewidth of our pulsed laser. We then scanned the four vibronic peaks previously measured with the improved resolution. This allowed us to measure the ground and excited state rotational constants. We used the unpublished ground state rotational measurements by NIST to improve the accuracy of our excited state constants. This spectroscopy is almost sufficiently precise to identify CaH⁺ in the solar spectrum. We plan to obtain a CW laser to achieve the required resolution. These results were published in J. Phys. Chem. A in Mar. 2018

We also have recently reviewed and summarized the state of molecular ion spectroscopy in Coulomb crystals. This work has been accepted as a Perspective article in J. Phys. Chem. Lett.

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Training Opportunities: This project provided training opportunities for a postdoc, two graduate students, and two undergraduates. The undergraduates were funded by other sources.

Both graduate students, Smitha Janardan and Aaron Calvin, were able to present their work at DAMOP 2017.

Molecular Simulations of Multi-Photon Dissociation of CaH⁺ and CaD⁺, Smitha Janardan, DAMOP 2017, Sacramento, CA, Jun. 5-9, 2017

Rovibronic Spectroscopy of Sympathetically Cooled 40CaH⁺, Aaron Calvin, DAMOP 2017, Sacramento, CA, June 5-9, 2017

Aaron Calvin also had the opportunity to give a hot topic presentation at the Conference on Cold and Controlled Molecules and Ions

Rovibronic Spectroscopy of CaH⁺ in a Coulomb crystal, Aaron Calvin, Conference on Colc and Controlled Molecules and Ions, Athens, GA Mar. 25-29, 2018

Results Dissemination: PI and students presented numerous presentations at scientific workshops and conferences.

Presentations by Prof. Brown

Quantum Computation with Molecular Ions, National Meeting of the American Chemical Society, New Orleans, LA, March 18, 2018

Spectroscopy of CaH⁺, Workshop on Cold Molecular Ions, Les Houces, France, May 29 – June 1, 2017

Presentations by Students

Molecular Simulations of Multi-Photon Dissociation of CaH⁺ and CaD⁺, Smitha Janardan, DAMOP 2017, Sacramento, CA, Jun. 5-9, 2017

Rovibronic Spectroscopy of Sympathetically Cooled 40CaH⁺, Aaron Calvin, DAMOP 2017, Sacramento, CA, June 5-9, 2017

Rovibronic Spectroscopy of CaH⁺ in a Coulomb crystal, Aaron Calvin, Conference on Colc and Controlled Molecules and Ions, Athens, GA Mar. 25-29, 2018

Two journal articles were published and a third article is in press.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI

Participant: Kenneth Brown

Person Months Worked: 1.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Aaron Calvin

Person Months Worked: 9.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

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as of 19-Mar-2019

National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Smitha Janardan

Person Months Worked: 3.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Jyothi Saraladevi

Person Months Worked: 8.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Undergraduate Student

Participant: Evan Reed

Person Months Worked: 3.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Undergraduate Student

Participant: Eric Pretzsch

Person Months Worked: 3.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

ARTICLES:

RPPR Final Report
as of 19-Mar-2019

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 3-Accepted
Journal: J. Phys. Chem. Lett.
Publication Identifier Type: **Publication Identifier:**
Volume: **Issue:** **First Page #:**
Date Submitted: 8/21/18 12:00AM **Date Published:**
Publication Location:

Article Title: Spectroscopy of molecular ions in Coulomb crystals

Authors: Aaron T. Calvin, Kenneth R. Brown

Keywords: molecular spectroscopy, molecular ions, coulomb crystals

Abstract: In this Perspective, we examine the use of laser-cooled atomic ions and sympathetically cooled molecular ions in Coulomb crystals for molecular spectroscopy. Coulomb crystals are well-isolated environments that provide localization and long storage times for sensitive measurements of weak signals and cold temperatures for precise spectroscopy. Coulomb crystals of molecular and atomic ions enable the detection of single photon molecular ion transitions at a range of wavelengths by a change in atomic ion fluorescence at visible wavelengths. We give an overview of the state-of-the-art from action spectroscopy to quantum logic spectroscopy for a wide range of molecular transitions from rotational sublevels separated by 10^{-7} cm⁻¹ to rovibronic transitions at 25000 cm⁻¹. We emphasize how this system allows for unparalleled control of the molecular ion state for precision spectroscopy with applications in astrochemistry and fundamental physics. We conclude with an outlook of ...

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

Acknowledged Federal Support: Y

DISSERTATIONS:

Publication Type: Thesis or Dissertation

Institution: Georgia Institute of Technology

Date Received: 21-Aug-2018

Completion Date: 10/17/17 7:41PM

Title: Simulation of multiphoton dissociation in calcium monohydride and calcium monodeuteride ions

Authors: Smitha Janardan

Acknowledged Federal Support: Y

Publication Type: Thesis or Dissertation

Institution: Georgia Institute of Technology

Date Received: 21-Aug-2018

Completion Date: 5/15/18 4:00AM

Title: Rovibronic spectroscopy of CaH⁺ in Coulomb crystals

Authors: Aaron T. Calvin

Acknowledged Federal Support: Y

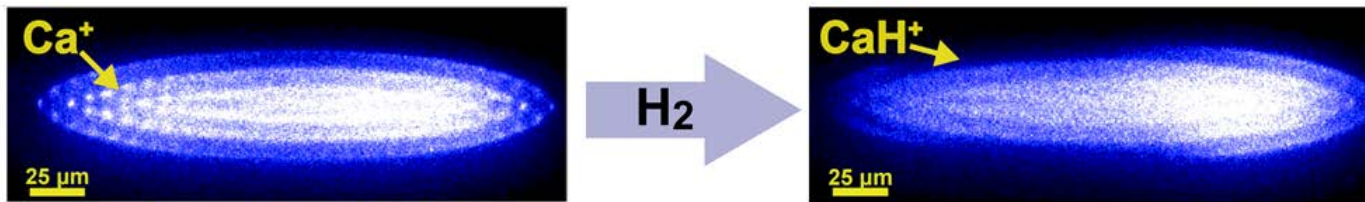
Control and Spectroscopy of Single Molecular Ions

Final Report Highlights

Kenneth Brown

W911NF1710071

Coulomb Crystals

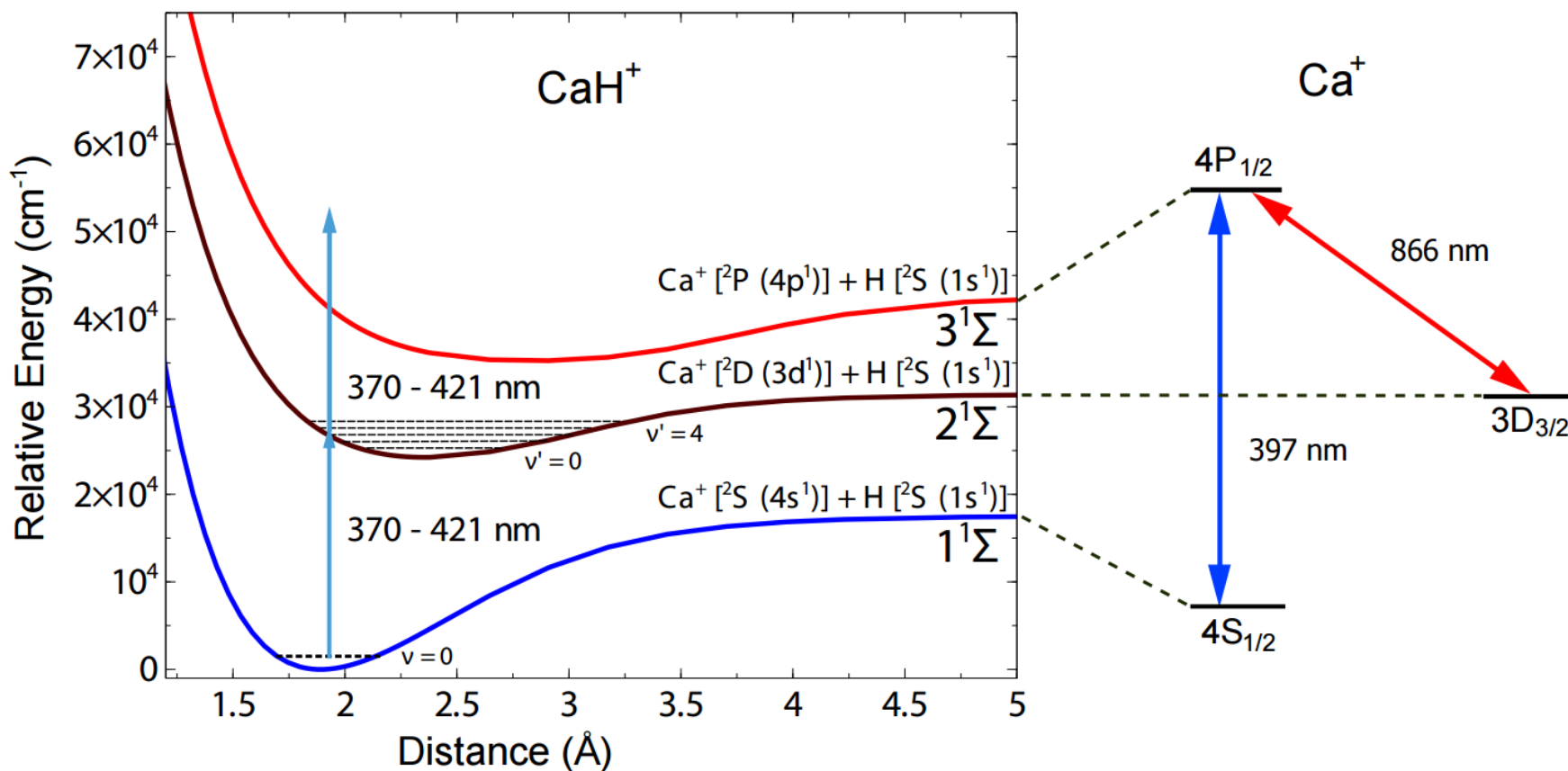


Molecular ions are sympathetically cooled by atomic ions to microkelvin temperatures

Radial potential is a pseudopotential (heavier ions are less confined)

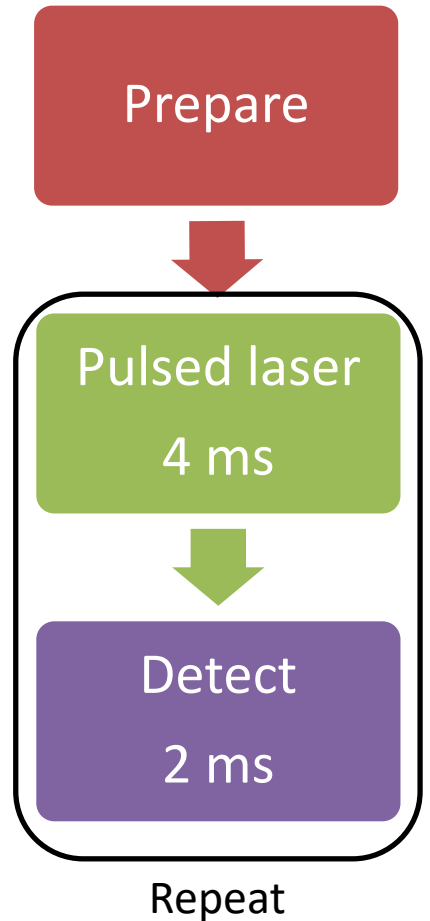
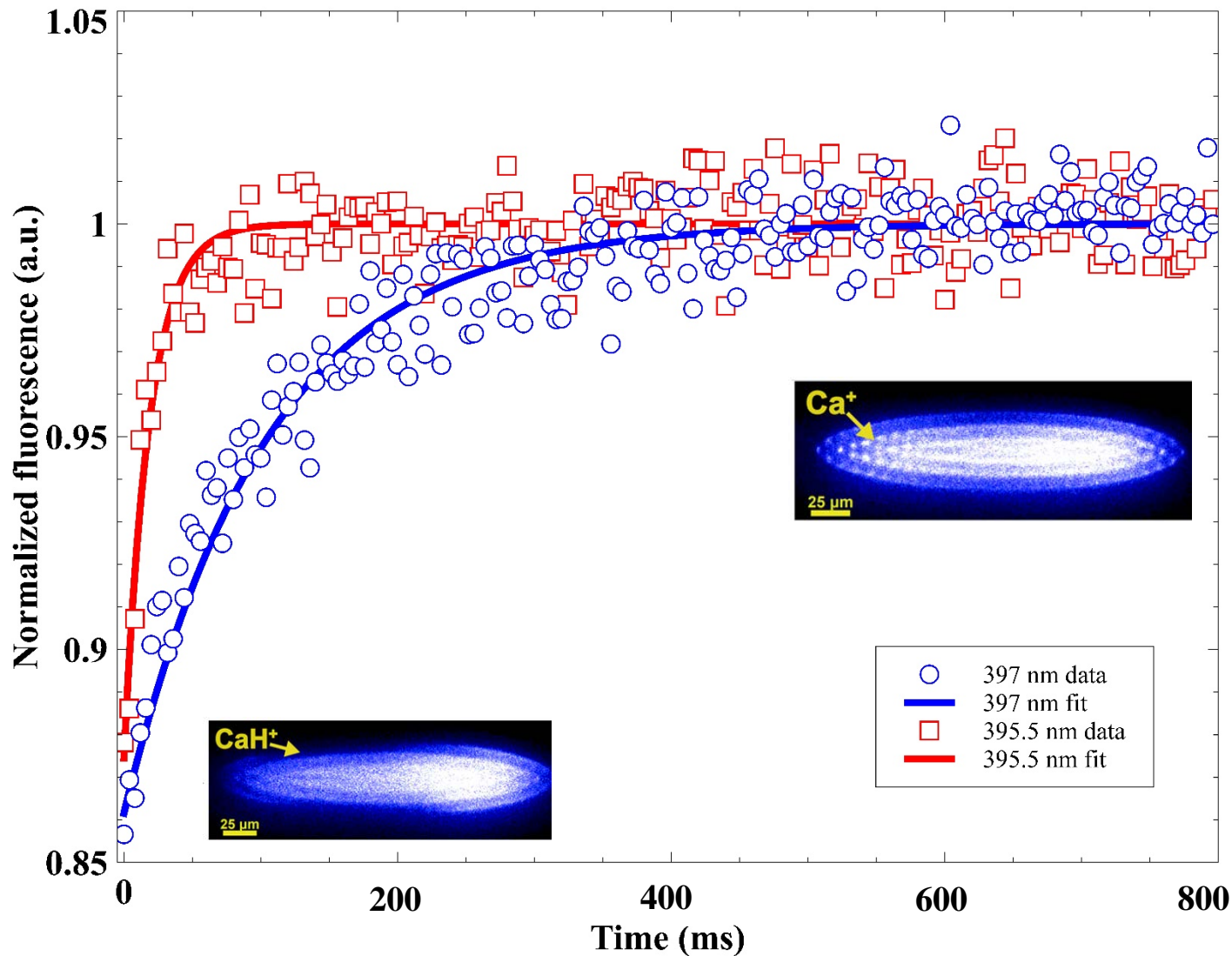
Optical force on laser-cooled ions pushes the directly cooled ions to one side

REMPD on electronic transition

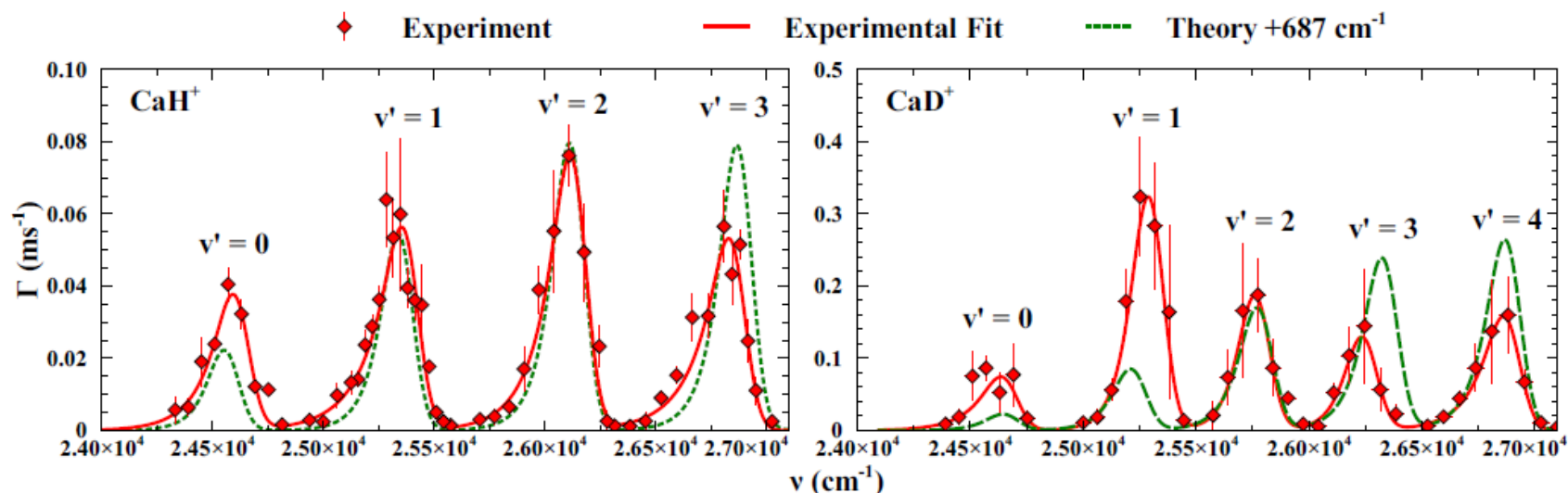


Resonance enhanced multi-photon dissociation of CaH^+ will result in the recovery of fluorescent Ca^+ . Rate of recovery as a function of dissociation wavelength can be used to determine spectrum.

Measure dissociation rate



REMPD in Coulomb Crystals: CaH^+



Vibronic spectroscopy of CaH^+

R. Rugango, et al. ChemPhysChem **17**, 3764 (2016)

Vibronic spectroscopy of CaD^+

J. Condoluci, et al. J. Chem. Phys. **147**, 214309 (2017)
(theory- CCSDTQ C. David Sherrill, GT)

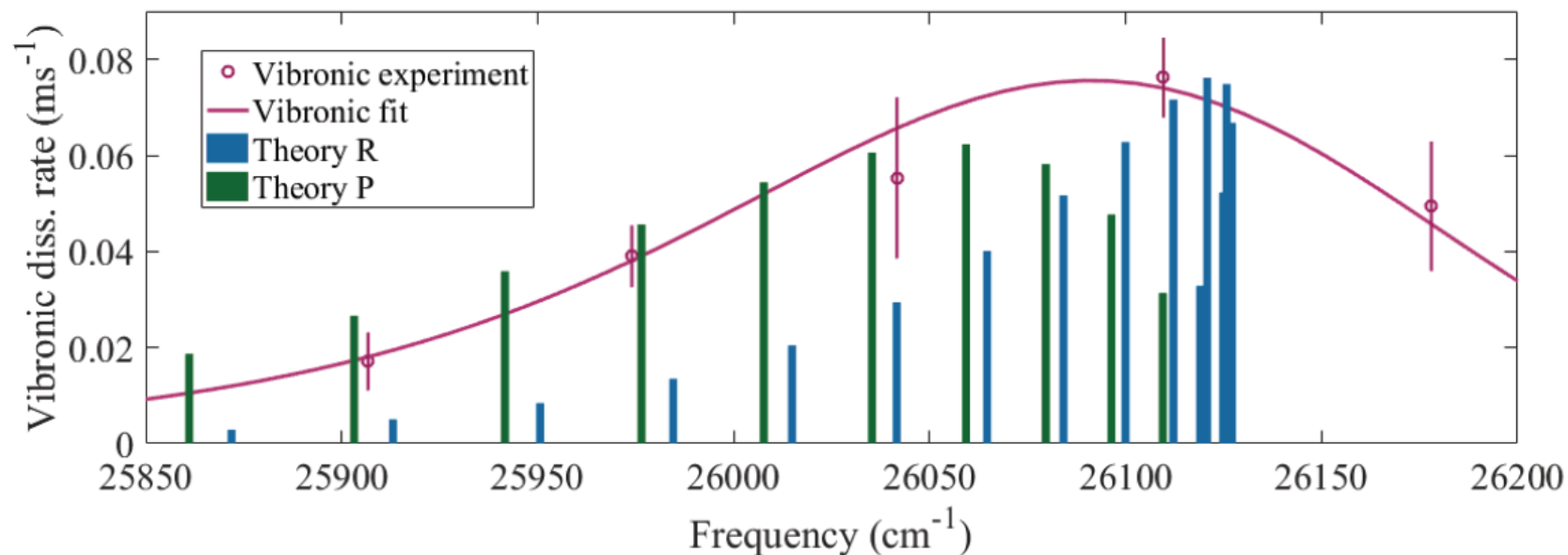
Published theory 687 cm^{-1} off

Revised theory 300 cm^{-1} off

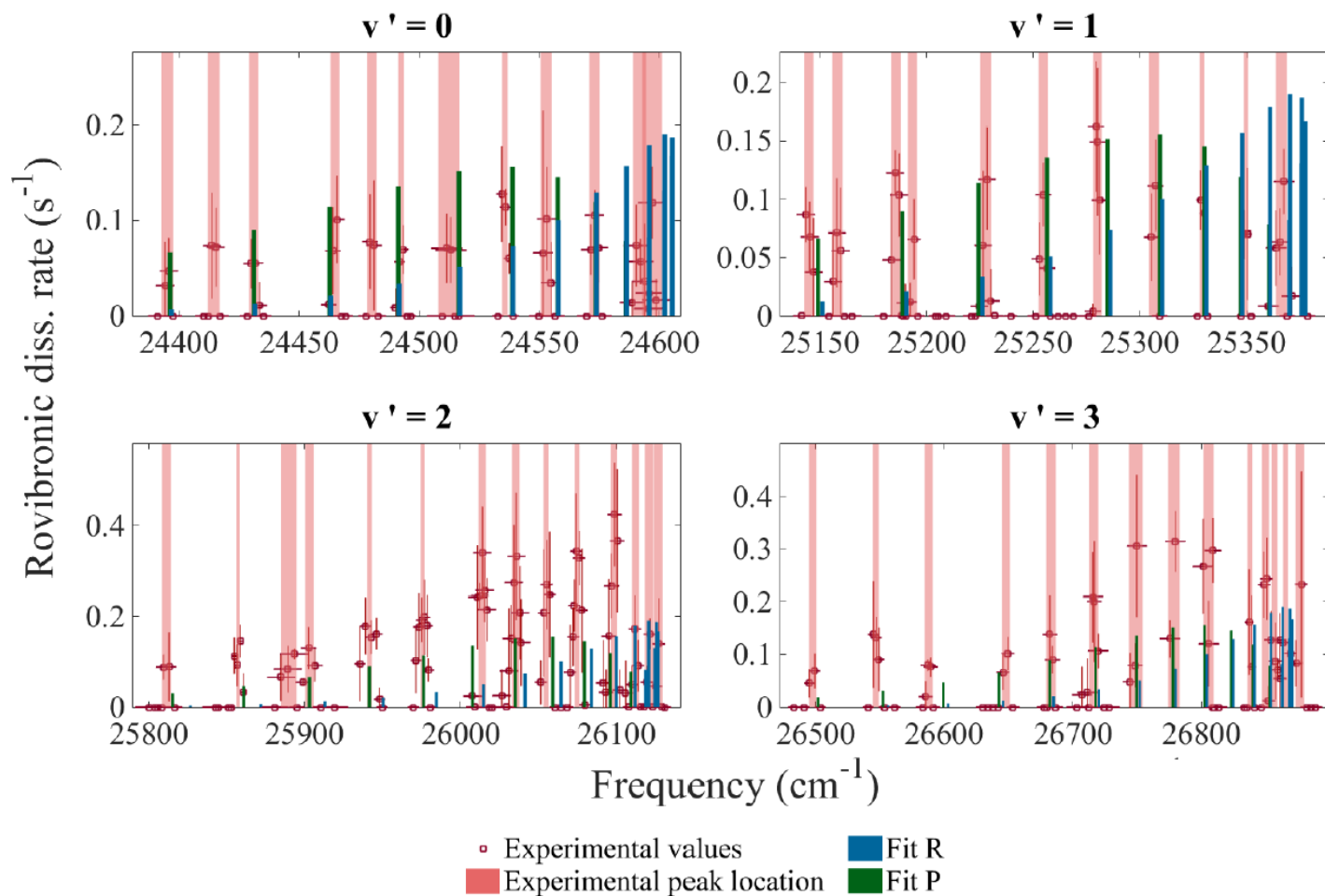
(needed to unfreeze 8 core electrons,
still need to add hyperfine and
non-Born Oppenheimer terms)

Underlying rotational structure

Vibronic peaks were a convolution of the underlying rovibronic transitions and laser bandwidth



Rovibronic transition



Rovibronic results

- Rovibronic spectroscopic constants are consistent with theory
- Resolution limited by pulse shaping method

v'	$\lambda(v')$	$B_{1,v'}$
0 Theory CCSDT	24294	3.047
0 Experiment	24595 ± 3	3.17 ± 0.08
1 Theory CCSDT	25073	3.00
1 Experiment	25370 ± 1.7	2.86 ± 0.03
2 Theory CCSDT	25861	2.94
2 Experiment	26119 ± 1.8	2.94 ± 0.05
3 Theory CCSDT	26655	2.88
3 Experiment	26863 ± 1.6	2.85 ± 0.03

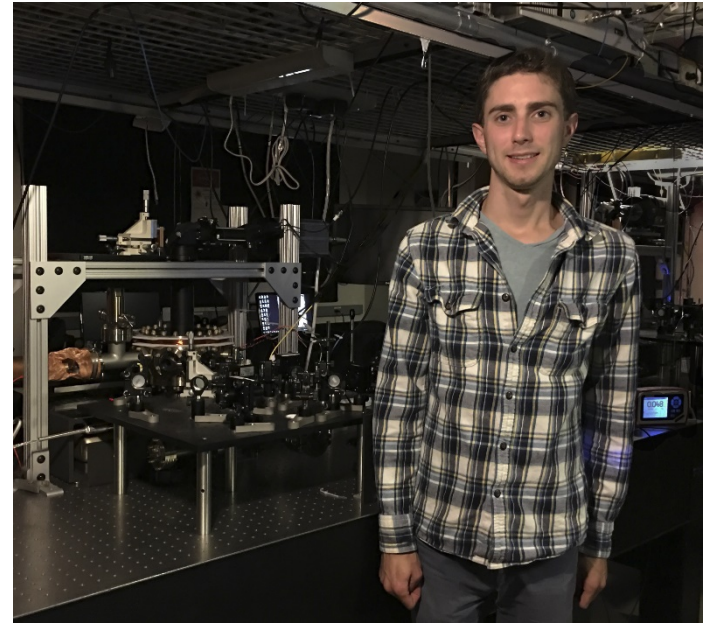
	CaH ⁺ Rovibronic	CaH ⁺ Vibronic	Theory
T(0,1)	24207 ± 2	24239 ± 5	23907
ω_1	786 ± 9.6	813 ± 6	772
$\omega\chi_1$	7.8 ± 2.3	16.8 ± 1.4	3.8

Used ground state rotational constants from NIST (C.W. Chou,private communication)

Training of PhD students



Smitha Janardan (PhD 2017)



Aaron Calvin (PhD 2018)