# COVER SHEET FOR PROPOSAL TO THE NATIONAL SCIENCE FOUNDATION

PROGRAM ANNOUNCEMENT/SOLICITATION NO./DUE DATE				Special Exce	Special Exception to Deadline Date Policy			FOR NSF USE ONLY	
NSF 14-579								NSF PROPOSAL NUMBER	
FOR CONSIDERATION BY NSF ORGANIZATION UNIT(S) (Indicate the most specific unit known, i.e. program, division, etc.)									
PHY - ATOMIC, MOLECULAR, AND OPTICAL EXPERIMENTAL PHYSICS									
DATE RECEIVED NUMBER OF COPIES DIVISION ASS			I ASSIGNED	SIGNED FUND CODE		Universal Numbering Syste	m) FILE LOCATION		
10/24/2017	1		03010000	РНҮ	1241	0669853	67	10/24/2017 9:16am	
EMPLOYER IDENTIFICATION NUMBER (EIN) OR       SHOW PREVIOUS AV         TAXPAYER IDENTIFICATION NUMBER (TIN)       Image: Comparison of the second secon			OUS AWARD NO.	RD NO. IF THIS IS IS THIS PROPOSAL BEING SUBMITTED TO ANOTHER FEDE AGENCY? YES □ NO ⊠ IF YES, LIST ACRONYM(S)			/ITTED TO ANOTHER FEDERAL YES, LIST ACRONYM(S)		
042103542					ENT-DAGED REINEWAL				
NAME OF ORGANIZATI	ON TO WHICH AWARI	SHOULI	D BE MADE	ADDRE	ADDRESS OF AWARDEE ORGANIZATION, INCLUDING 9 DIGIT ZIP CODE				
Amherst College				Amr Con	troller's Office				
AWARDEE ORGANIZAT	ION CODE (IF KNOWN)			Amł	nerst, MA. 0100	25000			
0021154000									
	ACE OF PERF			ADDRES	ss of primary pla nerst College	ACE OF PERF, IN	ICLUDING 9 DIGIT ZI	P CODE	
Amnerst College									
				Amf	0100, MA MA	25000 ,US.			
IS AWARDEE ORGANIZ	ATION (Check All That	Apply)	SMALL E	BUSINESS OFIT ORGANIZA		BUSINESS WNED BUSINES	S THEN CHECK HE	RELIMINARY PROPOSAL RE	
TITLE OF PROPOSED F	PROJECT RUI: Dr	iving F	orbidden	Vibrational (	Overtones in Tr	apped Mole	cular		
	Ions								
REQUESTED AMOUNT PROPOSED DURATION (1-60 MONTHS) REQUESTED STARTING DATE SHOW RELATED PRELIMINARY PROPOSAL NO						D PRELIMINARY PROPOSAL NO.			
\$ 514,119 36 months				07/01	1/18	IF APPLICABLE			
THIS PROPOSAL INCLU	JDES ANY OF THE ITE	MS LISTE	D BELOW		HUMAN SUBJE	CTS	Human Subjects As	surance Number	
	BBYING ACTIVITIES				Exemption Subse	ction or	IRB App. Date		
	RIVILEGED INFORMAT	ION				L ACTIVITIES: C	OUNTRY/COUNTRIE	S INVOLVED	
HISTORIC PLACES	ALSIACUC App. Date								
PHS Animal Welfare	Assurance Number					/E STATUS			
TYPE OF PROPOSA	∟ <u>Research</u>		1		Not a collabo	rative propo	sal		
PI/PD DEPARTMENT Physics & Astro	nomv		PI/PD POS Merri	stal address II Science Ce	ADDRESS ience Center				
	lioniy		Amhe	rst College	College				
413-542-5821 Amherst, M				rst, MA 0100 I Statos	MA 010025000 ates				
NAMES (TYPED)		High D	egree	Yr of Degree	Telephone Numb	er	Email Address		
PI/PD NAME									
David A Hanneke PhD			2008	413-542-552	5 dhann	eke@amherst.e	du		
CO-PI/PD									
CO-PI/PD									
CO-PI/PD									
CO-PI/PD									

Yes 🗖

# **CERTIFICATION PAGE**

## Certification for Authorized Organizational Representative (or Equivalent) or Individual Applicant

By electronically signing and submitting this proposal, the Authorized Organizational Representative (AOR) or Individual Applicant is: (1) certifying that statements made herein are true and complete to the best of his/her knowledge; and (2) agreeing to accept the obligation to comply with NSF award terms and conditions if an award is made as a result of this application. Further, the applicant is hereby providing certifications regarding conflict of interest (when applicable), drug-free workplace, debarment and suspension, lobbying activities (see below), nondiscrimination, flood hazard insurance (when applicable), responsible conduct of research, organizational support, Federal tax obligations, unpaid Federal tax liability, and criminal convictions as set forth in the NSF Proposal & Award Policies & Procedures Guide (PAPPG). Wilful provision of false information in this application and its supporting documents or in reports required under an ensuing award is a criminal offense (U.S. Code, Title 18, Section 1001).

#### Certification Regarding Conflict of Interest

The AOR is required to complete certifications stating that the organization has implemented and is enforcing a written policy on conflicts of interest (COI), consistent with the provisions of PAPPG Chapter IX.A.; that, to the best of his/her knowledge, all financial disclosures required by the conflict of interest policy were made; and that conflicts of interest, if any, were, or prior to the organization's expenditure of any funds under the award, will be, satisfactorily managed, reduced or eliminated in accordance with the organization's conflict of interest policy. Conflicts that cannot be satisfactorily managed, reduced or eliminated and research that proceeds without the imposition of conditions or restrictions when a conflict of interest exists, must be disclosed to NSF via use of the Notifications and Requests Module in FastLane.

#### Drug Free Work Place Certification

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent), is providing the Drug Free Work Place Certification contained in Exhibit II-3 of the Proposal & Award Policies & Procedures Guide.

#### Debarment and Suspension Certification (If answer "yes", please provide explanation.)

Is the organization or its principals presently debarred, suspended, proposed for debarment, declared ineligible, or voluntarily excluded from covered transactions by any Federal department or agency?

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) or Individual Applicant is providing the Debarment and Suspension Certification contained in Exhibit II-4 of the Proposal & Award Policies & Procedures Guide.

### Certification Regarding Lobbying

This certification is required for an award of a Federal contract, grant, or cooperative agreement exceeding \$100,000 and for an award of a Federal loan or a commitment providing for the United States to insure or guarantee a loan exceeding \$150,000.

### Certification for Contracts, Grants, Loans and Cooperative Agreements

The undersigned certifies, to the best of his or her knowledge and belief, that:

(1) No Federal appropriated funds have been paid or will be paid, by or on behalf of the undersigned, to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with the awarding of any Federal contract, the making of any Federal grant, the making of any Federal loan, the entering into of any cooperative agreement, and the extension, continuation, renewal, amendment, or modification of any Federal contract, grant, loan, or cooperative agreement.

(2) If any funds other than Federal appropriated funds have been paid or will be paid to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with this Federal contract, grant, loan, or cooperative agreement, the undersigned shall complete and submit Standard Form-LLL, "Disclosure of Lobbying Activities," in accordance with its instructions.

(3) The undersigned shall require that the language of this certification be included in the award documents for all subawards at all tiers including subcontracts, subgrants, and contracts under grants, loans, and cooperative agreements and that all subrecipients shall certify and disclose accordingly.

This certification is a material representation of fact upon which reliance was placed when this transaction was made or entered into. Submission of this certification is a prerequisite for making or entering into this transaction imposed by section 1352, Title 31, U.S. Code. Any person who fails to file the required certification shall be subject to a civil penalty of not less than \$10,000 and not more than \$100,000 for each such failure.

#### Certification Regarding Nondiscrimination

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is providing the Certification Regarding Nondiscrimination contained in Exhibit II-6 of the Proposal & Award Policies & Procedures Guide.

#### Certification Regarding Flood Hazard Insurance

Two sections of the National Flood Insurance Act of 1968 (42 USC §4012a and §4106) bar Federal agencies from giving financial assistance for acquisition or construction purposes in any area identified by the Federal Emergency Management Agency (FEMA) as having special flood hazards unless the:

- (1) community in which that area is located participates in the national flood insurance program; and
- (2) building (and any related equipment) is covered by adequate flood insurance.

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) or Individual Applicant located in FEMA-designated special flood hazard areas is certifying that adequate flood insurance has been or will be obtained in the following situations:

- (1) for NSF grants for the construction of a building or facility, regardless of the dollar amount of the grant; and
- (2) for other NSF grants when more than \$25,000 has been budgeted in the proposal for repair, alteration or improvement (construction) of a building or facility.

### Certification Regarding Responsible Conduct of Research (RCR)

## (This certification is not applicable to proposals for conferences, symposia, and workshops.)

By electronically signing the Certification Pages, the Authorized Organizational Representative is certifying that, in accordance with the NSF Proposal & Award Policies & Procedures Guide, Chapter IX.B., the institution has a plan in place to provide appropriate training and oversight in the responsible and ethical conduct of research to undergraduates, graduate students and postdoctoral researchers who will be supported by NSF to conduct research. The AOR shall require that the language of this certification be included in any award documents for all subawards at all tiers. No 🛛

# **CERTIFICATION PAGE - CONTINUED**

#### **Certification Regarding Organizational Support**

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that there is organizational support for the proposal as required by Section 526 of the America COMPETES Reauthorization Act of 2010. This support extends to the portion of the proposal developed to satisfy the Broader Impacts Review Criterion as well as the Intellectual Merit Review Criterion, and any additional review criteria specified in the solicitation. Organizational support will be made available, as described in the proposal, in order to address the broader impacts and intellectual merit activities to be undertaken.

#### **Certification Regarding Federal Tax Obligations**

When the proposal exceeds \$5,000,000, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Federal tax obligations. By electronically signing the Certification pages, the Authorized Organizational Representative is certifying that, to the best of their knowledge and belief, the proposing organization: (1) has filed all Federal tax returns required during the three years preceding this certification;

(2) has not been convicted of a criminal offense under the Internal Revenue Code of 1986; and

(3) has not, more than 90 days prior to this certification, been notified of any unpaid Federal tax assessment for which the liability remains unsatisfied, unless the assessment is the subject of an installment agreement or offer in compromise that has been approved by the Internal Revenue Service and is not in default, or the assessment is the subject of a non-frivolous administrative or judicial proceeding.

#### **Certification Regarding Unpaid Federal Tax Liability**

When the proposing organization is a corporation, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Federal Tax Liability:

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that the corporation has no unpaid Federal tax liability that has been assessed, for which all judicial and administrative remedies have been exhausted or lapsed, and that is not being paid in a timely manner pursuant to an agreement with the authority responsible for collecting the tax liability.

#### **Certification Regarding Criminal Convictions**

When the proposing organization is a corporation, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Criminal Convictions:

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that the corporation has not been convicted of a felony criminal violation under any Federal law within the 24 months preceding the date on which the certification is signed.

### **Certification Dual Use Research of Concern**

By electronically signing the certification pages, the Authorized Organizational Representative is certifying that the organization will be or is in compliance with all aspects of the United States Government Policy for Institutional Oversight of Life Sciences Dual Use Research of Concern.

AUTHORIZED ORGANIZATIONAL REP	SIGNATURE		DATE	
NAME				
Stephen M Nigro		Electronic Signature		Oct 24 2017 9:05AM
TELEPHONE NUMBER	EMAIL ADDRESS		FAX N	JMBER
413-542-2101	smnigro@amherst.edu		413	3-542-2223

### **Project Summary**

**Overview:** This project will investigate laser-driven transitions in trapped molecular ions. Such transitions have applications to precision measurements, optical frequency metrology, and searches for new physics. In this project, undergraduate students will contribute to the forefront of scientific research.

**Intellectual Merit**: This project will develop the tools needed to use vibrational transitions in molecules as precise optical frequency references and probes for time-variation of the proton-toelectron mass ratio. Such time-variation arises naturally in some theories of quantum gravity or dark matter. Molecular vibrations are promising places to look in next-generation searches.

The particular transition proposed here – from the ground vibrational state to the eleventh vibrationally excited state in  $O_2^+$  – has a narrow natural linewidth, high sensitivity to drifting constants, and long-term prospects as an optical molecular clock. It also has a transition frequency where optical measurement techniques are well developed. A key tool for this work is a stable optical local oscillator (a laser with wavelength 1063 nm) that is referenced to an iodine (I<sub>2</sub>) molecular clock.

This project builds on the PI's experience with trapped charged particles and precision measurements as well as existing infrastructure for trapping and cooling  $O_2^+$  molecules. A suite of experiments will demonstrate the promise of this system. First, two photons from the optical local oscillator will drive the transition, which will be detected by dissociating the molecule in a stateselective way. Second, the uncertainty in the absolute frequency of the transition will be reduced by a factor of approximately one million by comparison with a calibrated I<sub>2</sub> line. Third, continued comparison of the  $O_2^+$  clock with the I<sub>2</sub> clock over the course of a year will match or improve the best limit on changes in the proton-to-electron mass ratio that have been set in molecular systems. It will search for both drifts and oscillations in the ratio as a probe of additional dimensions, new scalar fields, and ultralight dark matter.

**Broader Impacts**: Precision spectroscopy impacts fields beyond atomic, molecular, and optical physics, including chemistry, astronomy, astrophysics, high-energy particle physics, and quantum gravity. Many of the techniques used here (trapping individual atoms and molecules, quantum state control) and larger themes (quantum gravity and dark matter) attract the interest of the general public.

The participation of undergraduates in the research program is integral to its success. Students will be introduced to active questions in the field and the experimental techniques being used to answer them. Many skills in experimental physics are transferable to a wide array of future endeavors. Students will present results through posters and presentations both locally and at conferences as well as write them up in journal articles and theses. Alumni of the PI's lab have gone on to success in top graduate programs. The project will also advance the career of a postdoctoral scholar.

# TABLE OF CONTENTS

For font size and page formatting specifications, see PAPPG section II.B.2.

	Total No. of Pages	Page No.* (Optional)*
Cover Sheet for Proposal to the National Science Foundation		
Project Summary (not to exceed 1 page)	1	
Table of Contents	1	
Project Description (Including Results from Prior NSF Support) (not to exceed 15 pages) (Exceed only if allowed by a specific program announcement/solicitation or if approved in advance by the appropriate NSF Assistant Director or designee)	15	
References Cited	9	
Biographical Sketches (Not to exceed 2 pages each)	2	
Budget (Plus up to 3 pages of budget justification)	6	
Current and Pending Support	1	
Facilities, Equipment and Other Resources	3	
Special Information/Supplementary Documents (Data Management Plan, Mentoring Plan and Other Supplementary Documents)	3	
Appendix (List below.) (Include only if allowed by a specific program announcement/ solicitation or if approved in advance by the appropriate NSF Assistant Director or designee)		

Appendix Items:

\*Proposers may select any numbering mechanism for the proposal. The entire proposal however, must be paginated. Complete both columns only if the proposal is numbered consecutively.

## **Project Description**

## 1 Introduction

We propose to investigate electric-dipole-forbidden vibrational overtones in trapped molecular ions. Such transitions have applications to precision measurements, optical frequency metrology, and searches for new physics. We will drive an overtone as a two-photon transition in a system that is of long-term interest as both an optical molecular clock and as a probe for time-variation of the proton-to-electron mass ratio.

Even simple molecules contain a rich set of internal degrees of freedom. If these internal states can be controlled at the quantum level, there are many applications to fundamental physics [1, 2] such as searches for new forces [3], investigation of parity [4, 5] and time-reversal [6, 7] symmetries, or searches for time-variation of fundamental constants [8–19]. Experiments with molecular ions [7,20–22] are already at the forefront of these scientific questions, taking advantage of the long interrogation times allowed in trapped systems.

In atomic systems, electric-dipole (E1) forbidden transitions play important roles as qubits [23– 25] and clocks [26, 27] due to their long lifetimes and narrow linewidths. These transitions in molecules have not been as exploited for precision measurements or reference transitions. In diatomic molecules with identical nuclei, all rotational and vibrational transitions within the same electronic potential are electric-dipole forbidden, offering a suite of narrow lines with frequencies from the radiofrequency to the optical. The nonpolar nature of the molecule suppresses systematic shifts related to electric fields, such as AC Stark shifts and blackbody radiation.

Some of these lines are particularly sensitive to variation in the proton-to-electron mass ratio  $\mu = m_p/m_e$ , which is predicted to change over time in many extensions to the standard model [2,28,29]. Some extensions predict a monotonic drift [28], but others involving ultralight dark matter suggest that  $\mu$  may oscillate with a frequency set by the mass of the dark-matter particle [29]. Models typically predict that the relative change of  $\mu$  should be of order 40 times larger than that of the fine-structure constant  $\alpha$  [28]. Current limits on present-day changes to  $\mu$  come from atomic clock experiments [30,31]. Nearly all the sensitivity to  $\mu$  variation comes from the hyperfine structure of cesium, and extracting the precise  $\mu$  dependence requires a model of the cesium nuclear magnetic moment [32]. The reliance on cesium clocks also means that atomic techniques are nearing their feasible limits, as the cesium microwave clock has been surpassed in stability by optical clocks [27] and is unlikely to improve by orders of magnitude in the near future. The vibration and rotation of molecules provide a model-independent means to search for variation in  $\mu$  [8–10,13,14,16]. Current limits set by molecules [33] are roughly three orders of magnitude less stringent than those set by atoms. We seek to continue developing molecular control techniques with an eye towards closing this gap.

We have already trapped  $O_2^+$  molecular ions and sympathetically cooled them to the Coulombcrystal state with co-trapped Be<sup>+</sup> atomic ions.

This proposal builds on our prior work and has these specific science goals:

- 1. Drive the E1-forbidden  $v=0 \rightarrow 11$  vibrational transition in  $O_2^+$  using two photons at 1063 nm.
- 2. Reduce the uncertainty on the measured transition frequency from several gigahertz to 10 kHz.
- 3. Repeat the measurement over the course of one year to set a limit on time-variation of the proton-to-electron mass ratio of  $\dot{\mu}/\mu < 6 \times 10^{-14} \text{ yr}^{-1}$ , which would match the current best measurement in a molecular system [33].

We chose the  $v = 0 \rightarrow 11$  transition because it has the long-term prospect [19, 34] of setting a limit several orders of magnitude tighter than the current best (Cs-clock-based) measurement  $\dot{\mu}/\mu < 10^{-16} \text{ yr}^{-1}$  [30, 31]. Further, high-power commercial lasers at 1063 nm are readily available and the techniques are well-developed for narrowing the laser's linewidth [27, 35–37], stabilizing it long-term [38, 39], and measuring its frequency against calibrated reference lines in iodine [40, 41].

This project will introduce undergraduate students to active questions in the field and the experimental techniques being used to answer them. It will advance the career of a postdoc, who will participate fully in the research program, work closely with the students, and join the community of scholars at Amherst College.

## 2 Results from Prior NSF Support

CAREER: Fundamental Physics Through Precision Measurements of Trapped Charged Particles June 1, 2013–May 31, 2018, \$600,000, Award PHY-1255170

At the beginning of our current grant, the PI was a relatively new assistant professor and was just setting up his lab. We had the electrodes for an ion trap, but only pieces of a vacuum chamber and parts for a laser system. During the award period, we built a versatile ion-trapping apparatus, built a novel laser for cooling beryllium ions [42], investigated candidate molecular ions for precision measurement experiments, wrote a paper on the favorable characteristics of the  $O_2^+$  molecule [18], and loaded mixed crystals of Be<sup>+</sup> atoms and  $O_2^+$  molecules. The goals of the current proposal directly extend our prior work.

The products of our prior support include two peer-reviewed papers [18,42], five undergraduate honors theses [43–47] with two more underway, two invited conference talks, two invited colloquium talks, and at least ten posters presented at DAMOP, undergraduate-focused conferences, or on-campus symposiums. This work has involved 19 undergraduate students and one postdoc.

### Intellectual merit of prior support

We have identified  $O_2^+$  as a molecule possessing a high sensitivity to present-day variation in the proton-to-electron mass ratio  $\mu$ .

We have also determined experimentally feasible means for measuring this time-variation. Searches for change in  $\mu$  usually involve monitoring the energy difference  $\hbar\omega$  between two energies with different  $\mu$  dependence,  $\hbar\omega = E'(\mu) - E''(\mu)$ . The fractional change in  $\mu$  is then related to an absolute frequency shift  $\Delta\omega$  through

$$\frac{\Delta\mu}{\mu} = \frac{1}{\mu} \left(\frac{\partial\omega}{\partial\mu}\right)^{-1} \Delta\omega = \left[\frac{\partial\omega}{\partial(\ln\mu)}\right]^{-1} \Delta\omega.$$
(1)

The quantity in square brackets is sometimes called the absolute enhancement factor because it correlates with a larger absolute frequency shift for a given fractional shift in  $\mu$ . The ideal system would have both a high absolute enhancement factor and the ability to resolve small absolute frequency shifts.

In molecules, both vibrational and rotational energies are sensitive to  $\mu$ . In particular, for a state of energy

$$E/(hc) = T_e + \omega_e \left( v + \frac{1}{2} \right) + B_e J(J+1),$$
(2)

the electronic energy  $T_e$  is independent of  $\mu$ , the vibrational coefficient  $\omega_e$  scales as  $\mu^{-1/2}$  and the rotational constant  $B_e$  scales as  $\mu^{-1}$ . (Here, the parameters are given as wave numbers. For scaling of additional coefficients, see Refs. [48–50].) Thus the absolute sensitivity of a particular state to variation in  $\mu$  is given by

$$\frac{1}{hc}\frac{\partial E}{\partial(\ln\mu)} = -\frac{1}{2}\omega_e(v+\frac{1}{2}) - B_e J(J+1).$$
(3)

Transitions between different vibrational states will generally yield higher sensitivity both because  $\omega_e$  tends to be larger than  $B_e$  and because selection rules preclude transitions between states of vastly different J. The first term in Eq. 3 shows a linear growth in the sensitivity with vibrational states. Thus, it is favorable to measure vibrational overtones rather than the  $v = 0 \rightarrow 1$  fundamental. As was pointed out in refs. [11, 12], anharmonicity in the potential decreases the sensitivity as the levels approach dissociation so there is a peak sensitivity at energies approximately 3/4 of the dissociation energy. The maximum sensitivity of a molecule is proportional to the potential depth, such that one should look for experimentally viable routes in deeply bound molecules.

As we point out in ref. [18], the  $O_2^+$  molecule has a deep electronic ground state potential  $(54\,600 \text{ cm}^{-1} = 6.8 \text{ eV})$  and a relatively simple molecular structure. It is homonuclear, so nuclear symmetry eliminates half the rotational states and forbids electric dipole (E1) transitions within an electronic state. Thus vibrational transitions should be very narrow-line because they decay primarily as electric quadrupole (E2) radiation. As discussed more thoroughly below, this nonpolarity also suppresses many systematic effects [12, 17–19, 34, 54] such as some AC Stark and blackbody radiation shifts. The most common isotope of oxygen  $(^{16}O, 99.8\%$  abundance) has no nuclear spin, so  $O_2^+$  lacks hyperfine structure. Unlike many molecular ions,  $O_2^+$  has measured spectroscopic parameters [51-53, 55-60] and existing theoretical calculations [61–65].

There are three main approaches to a  $\mu$ variation measurement in  $O_2^+$ . First, one could drive a vibrational transition directly. Although these are dipole-forbidden, they are quadrupole-allowed. The  $N_2^+$  ground-state v = $0 \rightarrow 1$  electric-quadrupole transition has been driven directly with a quantum cascade laser [21]. Similar techniques could be applied



Figure 1: Potential curves (in the Morse approximation) for the X, a, and A states of  $O_2^+$ . The horizontal lines indicate the measured energies of vibrational states [51–53]. Inset are the doublet-X and quartet-a levels closest to degeneracy, including spin–orbit splittings. The labels on each fine-structure level indicate  $\Omega$  in the case (a) (low-J) limit. From ref. [18].

ser [21]. Similar techniques could be applied to  $O_2^+$ . We do not choose this approach because

the laser sources (at 5.3  $\mu$ m for  $O_2^+$ ) are not yet available with narrow linewidths and thus our ability to resolve  $\Delta \omega$  in eq. 1 is compromised. Attempts to drive transitions to v > 1 suffer from very small quadrupole moments. A second approach is to drive the vibrational overtones as twophoton transitions. This is the approach we adopt and discuss below. A third approach relies on an accidental degeneracy between several excited vibrational states of the ground  $X^2 \Pi_g$  potential and low vibrational states of the excited  $a^4 \Pi_u$  potential [18], as shown in fig. 1. This degeneracy brings states with different  $\mu$ -sensitivity within radio or microwave frequency of each other. It has the potential for high absolute sensitivity while requiring only modest relative precision. It is an intriguing prospect, but the two-photon vibrational overtone approach looks favorable at this point for both technical and systematics-related reasons.

> We have built an apparatus that can load beryllium atomic ions for sympathetic cooling of co-trapped molecular ions.

The cooling transition in  $Be^+$  is at 313 nm, and we have built this UV laser using a unique design of third-harmonic generation of a 940-nm infrared laser (see fig. 2). We have published a manuscript [42] describing the system and demonstrating its use in laser cooling and detecting  $Be^+$  ions and sympathetically cooling molecular ions. Our system's maximum output power of 36 mW is more than needed for simple Doppler cooling. Though we will not need to sideband cool for the work in this proposal, our system has that capability, which will be helpful in the long term.

Our source for  $Be^+$  ions is thermal emission from a beryllium wire. We currently ionize the atoms via electron-impact. We are in the process of constructing a 235-nm laser that will resonantly photoionize beryllium [66]. We are using a new design that frequency-doubles a 470-nm diode laser. The blue laser diodes are only recently available and allows for a simpler system than the more traditional fourthharmonic-generation of an IR diode laser [67]



Figure 2: Schematic of the Be<sup>+</sup> cooling laser system. For simplicity, it omits many mirrors, lenses, and diagnostic and control electronics. From ref. [42].

or the third-harmonic [68–70] or fourth-harmonic-generation [71] of a pulsed Ti:Sapphire laser. We are on track for completing this new photoionization laser in January 2018, and expect to write a manuscript describing its use. Besides enhancing the efficiency and cleanliness of our Be<sup>+</sup> loading, the 235-nm laser will play an important role as a photodissociation laser for  $O_2^+$ , which is discussed below.



Figure 3: Two types of ion crystals in our trap. The upper (a) is pure Be<sup>+</sup>. The lower (b) is a mix of Be<sup>+</sup> and  $O_2^+$ , where the molecules appear as non-fluorescing gaps in the crystal. The trap parameters were different in these two cases, yielding slightly different aspect ratios and ion densities.



Figure 4: (2+1) REMPI of neutral oxygen. The lower X and d states are in neutral O<sub>2</sub>, while the others are in the ion O<sub>2</sub><sup>+</sup>.

We have loaded  $O_2^+$  molecules into Coulomb crystals.

Figure 3 shows such a mixed crystal of Be<sup>+</sup> and  $O_2^+$ . Our vacuum chamber includes a precision leak valve (Lesker VZLVM29) for controlled admittance of gas such as  $O_2$ . Our initial loading was via electron-impact ionization. This is not state-selective and the nonpolar  $O_2^+$  does not thermalize readily with blackbody radiation (BBR). (Indeed, this immunity from BBR is a feature for us.) So we are moving to a 2+1 resonance-enhanced multiphoton ionization (REMPI) scheme (fig. 4). By use of REMPI, we will have vibrational selectivity and load ions into only a few rotational states. A frequency-doubled pulsed dye laser (Quantel TDL60) generates 10-ns pulses of energy 0.25 mJ near 301 nm. These pulses excite a two-photon transition from the neutral oxygen  $X^{3}\Sigma_{g}^{-}$ state to the Rydberg  $d^{1}\Pi_{g}$  state [72–74]. A third photon ionizes that state. (The third photon is likely from the same pulse, but the beryllium cooling and photoionization lasers have enough energy as well.) Because the Franck-Condon factors between the neutral  $d^{1}\Pi_{g}$  and ion  $X^{2}\Pi_{g}$ states are nearly diagonal, we have complete vibrational selectivity. Because the transition to the neutral  $d^{1}\Pi_{g}$  is rotationally resolved, selection rules constrain the final ion state to be in only a few rotation states [75, 76].

### Intellectual merit of prior support – educational plan

The CAREER grant included an educational plan as an integral component. In addition to student involvement in research, discussed below, I collaborated with other members of my department to revise the physics major curriculum. Our revision emphasized maintaining high-quality instruction while adding flexibility in the required coursework and a renewed emphasis on experimental work. As an example of such a change, I revised our sophomore-level lab course with an eye toward quality over quantity. Students now go in-depth over several weeks on an experiment instead of changing topics each week. I shifted the writing emphasis from producing 12–13 unique lab reports to additional instruction on scientific communication, including time for peer review and revision. In our introductory-course labs, we have added multi-week projects on topics of the students' own design. We have just added a new introductory-level course on oscillations and waves.

#### Broader impacts of prior support

The participation of undergraduates in the research program has been integral to its success. During the prior grant, 19 undergraduate students participated on the work. Of these, 11 worked through the summer, five completed a senior honors thesis [43–47], and two are currently working on a thesis. Students in my lab have designed and built external cavity diode lasers, scanning Fabry Perot cavities, microcontroller-based experiment sequencers, and a variety of electronics and computer-programming projects. They have done experiments with Be<sup>+</sup> ions to characterize trapping parameters and determine the mass of co-trapped molecular ions. They have done theoretical calculations for practical things like nonlinear optics, searched the literature for candidate molecules for constants-variation experiments, and calculated molecular photo-ionization rates including all the spherical-tensor algebra.

Thesis students in my lab have continued to graduate school in physics, electrical engineering, and related fields at Stanford, Scripps Institution of Oceanography, Dartmouth, Princeton, Caltech, and Harvard. Current senior Alexander Frenett won a Goldwater Scholarship based on work in my lab and his considerable promise.

Beyond instruction for lab skills specific to their projects, I have trained each student in research techniques such as data handling and analysis, the responsible conduct of research, and how to search and read the literature. I closely mentor each student as they work with me. Over the summer, Amherst College provides a variety of programming such as to scientific communication, how to use various software packages (e.g. Mathematica or Python), and research ethics.

My students have opportunities to present their work publicly. Several students have joined me at DAMOP to help present our group's poster and to learn about our field. Summer students present posters at a symposium on campus in early fall. Thesis students give two public lectures on their work and write substantial documents [43–47]. Alexander Frenett presented a poster at the NSF-sponsored Optics and Photonics Winter School at the University of Arizona. Lauren Weiss won an award for her poster at the NSF-sponsored Emerging Researchers National (ERN) Conference in STEM. Six students are co-authors on refereed publications [18,42].

My prior support funded a two year term for a postdoc. Dr. Ryan Carollo has been a valuable member of our group, and I have given him opportunities both to demonstrate his skills and to grow as a scholar during this phase of his career. He has worked closely with our students. He attended and/or presented at DAMOP and the North American Conference on Trapped Ions (NACTI). He has been a co-author of two papers [18, 42] and the first author on one [42].

It is difficult to separate the Intellectual Merit and Broader Impacts of the educational component of my CAREER grant. Much of our curricular revision was done with an eye toward increasing the diversity of our physics majors to take advantage of the diverse student body at Amherst College. Our department (and I personally) have worked closely with the Amherst Association of Women in Science as well as a new initiative called Being Human in STEM. Our resulting actions include curriculum-scale changes such as increasing the flexibility of our major requirements through electives as well as classroom-scale changes such as implementing values-affirmation exercises in our introductory courses. These exercises have been shown [77] to reduce gender achievement gaps in such courses.

### **3** Intellectual Merit

### Vibrational overtones

Spectroscopy and control of molecular vibrational states could improve our knowledge of fundamental physics and lead to better optical clocks. Vibrational overtones (transitions with  $|\Delta v| > 1$ ) have been driven with one photon in several heteronuclear molecular ions, such as <sup>40</sup>CaH<sup>+</sup> [78] and HD<sup>+</sup> [22]. In homonuclear ions, such transitions are electric-dipole forbidden. Because their only decay mechanism is through quadrupole radiation, these transitions should have extremely narrow linewidths. In principle, it is possible to drive such vibrational transitions at higher order, and the  $v = 0 \rightarrow 1$  transition has been driven in N<sub>2</sub><sup>+</sup> as an electric quadrupole *E*2 transition [21]. For overtone transitions, the quadrupole moment rapidly vanishes. Instead, it is possible to drive them as a two-photon transitions. Two-photon transitions are used, for example, in the forbidden 1*S*-2*S* transition in atomic hydrogen [79,80].

The homonuclear molecule  $O_2^+$  is a good system for developing techniques for quantum control of molecular vibrational states. Table 1 lists some vibrational levels of  $O_2^+$  and several parameters relevant for driving two-photon transitions from v = 0 and for other parts of our proposal. Spectroscopy of  $O_2^+$  has been undertaken for many years [51–53,55–60] in part because of the important role it plays in the ionosphere of Earth and other planets [81]. The most relevant spectroscopy for our needs comes from high-resolution emission spectra [58] and VUV-laser-excited, pulsed-fieldionization photoelectron spectra [51]. They give uncertainties on the vibrational transitions at the few-gigahertz level.

v'	$\lambda$	$\frac{-1}{2\pi} \frac{\partial \omega}{\partial (\ln \mu)}$	$\frac{\Omega/(2\pi)}{I}$	PD $\lambda$	v'	$\lambda$	$\frac{-1}{2\pi} \frac{\partial \omega}{\partial (\ln \mu)}$	$\frac{\Omega/(2\pi)}{I}$	PD $\lambda$
	(nm)	(THz)	$(10^{-6} \frac{\text{Hz}}{\text{W/m}^2})$	(nm)		(nm)	(THz)	$(10^{-6}  \frac{\text{Hz}}{\text{W/m^2}})$	(nm)
1	10614	28	1.5	113	11	1063	249	2.0	238
2	5386	54	2.3	123	12	984	266	1.9	257
3	3617	80	1.6	133	13	917	281	2.2	277
4	2738	104	1.7	144	14	860	296	2.1	299
5	2211	128	1.7	155	15	810	310	2.5	324
6	1859	151	1.5	166	16	767	323	2.5	352
7	1609	172	1.8	179	17	730	334	2.8	$381^{*}$
8	1421	193	1.6	192	18	696	345	2.9	$401^{*}$
9	1275	213	1.9	206	19	667	355	3.2	$423^{*}$
10	1158	231	1.7	221	20	640	364	3.6	$446^{*}$

Table 1: Parameters for the first 20 vibrational transitions from v'' = 0 to v', driven as twophoton transitions at wavelength  $\lambda$ . Also given are the absolute sensitivity of the transition to  $\mu$ -variation, the Rabi frequency as a function of laser intensity, and the optimal wavelength for a photodissociation (PD) laser. For transitions with v' > 17, the best Franck-Condon overlap would drive a transition to a bound state, so the energy to the continuum is given instead with an asterisk<sup>\*</sup> marking the change.

We have chosen the transition

$$|X^{2}\Pi_{g,1/2}, v'' = 0, J'' = \frac{1}{2}\rangle \leftrightarrow |X^{2}\Pi_{g,1/2}, v' = 11, J' = \frac{1}{2}\rangle$$
(4)

because it has the best mix of sensitivity to variation in  $\mu$ , available laser technology (1063 nm), and nearby calibrated reference transitions [40,41]. Driving this overtone transition instead of the fundamental increases the sensitivity by almost a factor of nine, as one would expect from eq. 3. (It is nine not eleven because we have accounted for additional anharmonic terms [11,12].) Moving farther up the ladder to v' = 20 would increase the sensitivity by another 50%, but at the cost of more complex or lower power lasers and fewer options for absolute frequency calibration. Our choice of  $J = \frac{1}{2}$  is motivated by suppression of Zeeman and electric quadrupole systematic effects, which we discuss below.

### Experimental procedure

Our experimental goals are to drive the  $v = 0 \rightarrow 11$  transition, measure its frequency to 10 kHz accuracy, and repeat the measurement over the course of one year to set the limit  $\dot{\mu}/\mu < 6 \times 10^{-14}$ . The general procedure for each of these goals is similar.

- 1. Load approximately 50  $\mathrm{Be^+}$  and  $\mathrm{O}_2^+$  ions through photoionization and cool to a Coulomb crystal
- 2. Probe the  $v = 0 \leftrightarrow 11$  transition at  $2 \times 563\,943$  GHz (1063.20 nm or 18811.1 cm<sup>-1</sup>/2)
- 3. Photodissociate the v = 11 state to  $O + O^+$  through the excited  ${}^{2}\Sigma_{u}^{+}$  state
- 4. Dump the trap and analyze the ions with time-of-flight mass spectrometry

We have the computer and data-acquisition hardware in place for these experiments. This includes a hardware-based sequencer, flexible direct-digital synthesis (DDS) rf systems with real-time amplitude, frequency, and phase control, and a hybrid LabVIEW/Python experiment programming software. We discuss each experimental step below and show the probe and dissociation steps in fig. 5.

Photoionization of beryllium is through a resonant excitation of the neutral at 235 nm [66–71]. This laser is the honors thesis project of Christian Pluchar, and we anticipate its completion in January 2018. Photoionization of oxygen is a 2+1 REMPI scheme [72–74]. We have the frequency-doubled pulsed dye laser required for this scheme. For our initial experiments, we will load from 300 K background gas leaked into our chamber at pressures around  $10^{-9}$  mbar. By tuning the dye laser such that



Figure 5: Two-photon probe and one-photon photodissociation transitions

it resonantly excites the neutral oxygen Rydberg state  $|d^{1}\Pi_{g}, v = 0, J = 1\rangle$ , we will ensure ion populations only in the  $|X^{2}\Pi_{g}, v = 0, J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}\rangle$  states. The vibrational selectivity is high

because of diagonal Franck-Condon factors between the ion state and the neutral Rydberg state. With only one pulsed laser, we will necessarily excite J's other than our target  $J = \frac{1}{2}$  [75,76]. This will eat into our signal, but will not effect the measurement for those ions that are in the correct state. It is possible that ions in the other states could be used for diagnostics such as magnetic field or laser intensity calibrations. We will use ion crystals of approximately 50 ions in order to increase our signal and duty-cycle. Our target precision is not yet at a level where micromotion or other off-axis effects must be avoided entirely (see systematics discussion below).

We will probe all  $O_2^+$  ions simultaneously. The Rabi frequency of the two-photon transition may be estimated by second-order perturbation theory with the transition driven off-resonantly "through" the excited  $A^2\Pi_u$  state. Electric-dipole transition moments, Franck-Condon factors and other parameters are tabulated in ref. [82], based on fits to experimental data. From them, we estimate the Rabi frequencies in table 1. For a 1 kHz Rabi frequency and a 100  $\mu$ m waist, we require a power of 8 W. For each  $\mu$ -variation experiment, we will time-stamp the probe pulse so that the data can be analyzed for oscillations in  $\mu$  [29] not just drifts. We have a GPS receiver that will allow accurate time recording, as in ref. [83].

To determine whether an ion has made the transition, we will photodissociate the  $|X^2\Pi_g, v = 11\rangle$  state to the continuum of the  ${}^{2}\Sigma_{u}^{+}$  state. This electronic state shares the same  $O({}^{3}P_{g}) + O^{+}({}^{4}S_{u})$  dissociation channel with the X state, but it has a much shallower potential and its potential minimum is significantly offset [62, 65], as shown in fig. 5. Using the potential's parameters from an *ab initio* calculation in ref. [65], we estimate the energy of a dissociating transition that has the maximum Franck-Condon overlap. That is, we calculate the energy difference between the X potential at the outer turning point of each vibration level and the  ${}^{2}\Sigma_{u}^{+}$  potential at the same internuclear separation. The results are included in table 1. For our target level v = 11, that energy corresponds to a laser at 238 nm. Our 235 nm beryllium photoionization laser is well matched, and the Franck-Condon overlap is still favorable at that wavelength. We anticipate photodissociation to be a much faster process than other state-detection techniques, such as laser-induced charge transfer with a background gas [84, 85].

In order to count the number of  $O_2^+$  ions versus  $O^+$  ions (and thus the fraction of ions in v = 0 versus 11), we need to analyze the masses of the ions in the trap. Our current technique involves probing the crystal trapping parameters such as resonant excitation of the ions' normal modes [86, 87] or taking the Paul trap's mass-dependent a and q parameters into the instability region for one mass but not another [88–90]. In this way, we have been able to distinguish  $O_2^+$  (mass 32 amu),  $O^+$  (16 amu, which we have loaded by electron-impact dissociation), and  $Be^+$  (9 amu). Other molecular ion experiments have relied on techniques such as comparing ion-crystal images with simulation [21, 85]. Time-of-flight mass spectrometery (ToF-MS) [91–97] is a faster way to analyze the trap contents and has unit detection efficiency. In it, a voltage pulse extracts the ions from the trap and sends them down a field-free drift region to be detected by a microchannel plate (MCP) detector. The extraction field adds the same energy to each ion such that the lighter ones are moving faster. Thus, detection time correlates with mass. This technique is destructive, but photodissociation is as well. Alexander Frenett is currently constructing our ToF-MS as part of his honors thesis project. We anticipate testing it in a separate vacuum chamber in spring 2018 and installing it in the main chamber with the trap during year one of this grant. Our massresolution needs are modest (resolving masses 9, 16, and 32 amu), but we are designing our system such that it can easily resolve Be<sup>+</sup> from BeH<sup>+</sup>, which is an occasional contaminant ion. This corresponds to  $m/\Delta m = 10$ , which again is quite modest compared to others' published results such as  $m/\Delta m = 50$  [92], 100 [95], 500 [96], and 1100 [97].



Figure 6: Overview of our probe laser system at 1063 nm. It is stabilized on short- to medium-timescales with a ULE cavity and referenced long-term to a molecular transition in  $I_2$ .

### Laser source at 1063 nm

The laser used to drive the two-photon transition must be a well-stabilized optical frequency source. Fig. 6 gives an overview of the system we intend to assemble. Because the only decay mechanism of the v' = 11 level is quadrupole radiation, the transition linewidth will be entirely set by the probe laser. The equipment budget of this proposal is mostly for acquiring the source and requisite materials to stabilize and amplify it. We plan to use a tunable diode laser as our master oscillator. While a fiber laser has an intrinsically narrower linewidth, diode lasers are more tunable and are available with more output power (200 mW); we plan on actively stabilizing the laser. We opt for a commercial diode laser to take advantage of the engineering that has gone into making it more stable and robust (e.g. ref. [98]).

For short- to medium-term stability, we will stabilize the laser with an ultra-low expansion (ULE) Fabry-Perot cavity [27, 35–37]. While it is possible to narrow optical sources to sub-hertz linewidths [37, 99], we will not need to go to such lengths. Our target precision of  $\dot{\mu}/\mu < 6 \times 10^{-14} \text{ yr}^{-1}$  corresponds to a frequency precision of  $2 \times 10^{-14}$ , which is 6 Hz at 1063 nm. (Note that we will not have to measure the absolute frequency in hertz to that level; see the measurement discussion below.) We can estimate the required linewidth with a simple calculation. With a laser of linewidth  $\Gamma$ , probe times equal to  $\Gamma^{-1}$ , N ions, and total experiment duration  $\tau$ , we would expect a statistical uncertainty  $\delta \omega \sim \sqrt{\Gamma/(N\tau)}$ , assuming our signal-to-noise ratio is limited by quantum projection noise [100]. For example, a laser of linewidth 1 kHz probing 10 ions would reach our required 6 Hz in 0.4 s. We intend to shoot for a sub-100 Hz linewidth, which will enable the option of longer probe times and/or lower powers because of increased laser coherence. This will require a high-finesse, temperature-stabilized, ULE cavity but likely not any active vibration suppression.

### Absolute calibration with $I_2$

Ideally, optical frequency measurements like the one proposed here are referenced to other optical clocks [27, 101-104] via a frequency comb [105]. That level of precision is not yet needed to hit the target of this proposal. Instead, we will double the master laser to 531.60 nm and reference it to molecular iodine. The doubling will be single-pass in a commercial fiber-coupled periodically polled lithium niobate waveguide doubler. These devices have specified conversions of 100 %/W up to 100 mW input [106], which corresponds to 100 mW in the infrared converting to 10 mW in the

green. They can be used at even higher input powers [107, 108], but this level of green light will suffice for I<sub>2</sub> and 100 mW of IR will be available in our setup before the amplifier. The conversion is single-pass with no feedback required except to temperature-stabilize the crystal.

Using iodine as an optical frequency reference is a well-developed technique [38, 39, 109]. With a room-temperature gas of iodine, there are tabulated references lines through the 499–676 nm range [40]. Our setup will use modulation-transfer spectroscopy, which yields sub-Doppler linewidths, is free of any Doppler shift, and gives a nearly flat baseline [110–112]. Many such systems have been built near 532 nm (doubled Nd:YAG), and they are able to achieve parts in  $10^{14}$  or better with few-second integration times [38,39,109].

In order to achieve long-term stability, systematic effects in the iodine cell must be controlled. The largest such affects are pressure shifts and light-pressure shifts. The pressure in our iodine cell will be controlled via the vapor pressure [113] of a sample of crystalline iodine in a cold finger. Vapor pressures of 0.8-0.4 Pa would require temperatures of -15 C to -20 C for the cold finger [38]. Measured pressure shifts are on the order -3 kHz/Pa [39,112], which would correspond to roughly 200 Hz/K. To keep an absolute stability of 12 Hz (6 Hz in the IR) would require cold-finger stability at the level of 0.06 K. Light-pressure shifts seem to change with experiment-specific effects such as wavefront curvature, but are of the order of 1 kHz/mW [39,112]. With a 1 mW pump beam, we would require 1 % power stability.

Our  $\dot{\mu}$  experiment does not require calibrating the  $O_2^+$  transition frequency in hertz as long as we have a stable reference source. In this case, we will simply measure the frequency offset from a particular iodine line (lines numbered 1193 and 1194 in ref. [40] are within our  $O_2^+$  line's uncertainty) over time. It turns out that another nearby line (number 1209) has been measured with an accuracy of 8 kHz by use of a cesium-calibrated frequency comb [41]. We will use this iodine line to measure our  $O_2^+$  transition to a similar level in hertz (goal 2 of this proposal). The ULE cavity's 1.5 GHz free-spectral range will provide a stable frequency reference for bridging the approximately 132 GHz offset.

### Measurement of $\dot{\mu}/\mu$

The most sensitive measurement of  $\dot{\mu}/\mu$  in a molecular system used a carbon-dioxide laser near 10  $\mu$ m to measure a rovibrational transition in a beam of SF<sub>6</sub>. By use of a frequency comb and a cesium fountain clock, they tracked the SF<sub>6</sub> frequency versus the cesium hyperfine frequency over the course of two years. They set the limit  $\dot{\mu}/\mu = (-3.8 \pm 5.6) \times 10^{-14} \text{ yr}^{-1}$  [33]. We aim to match or improve this limit. By using a 10-times higher transition frequency, we will not need subhertz optical frequency measurement (their resolution was 0.8 Hz). By comparing our frequency to another optical reference (I<sub>2</sub> rovibrational/electronic transition vs. Cs hyperfine transition), we will not need access to an atomic fountain to achieve parts in 10<sup>14</sup> precision. The O<sub>2</sub><sup>+</sup>  $v = 0 \leftrightarrow 11$  transition's absolute sensitivity to changes in  $\mu$  is  $\frac{1}{2\pi} \frac{\partial \omega}{\partial(\ln \mu)} = -249$  THz.

The  $O_2^+ v = 0 \leftrightarrow 11$  transition's absolute sensitivity to changes in  $\mu$  is  $\frac{1}{2\pi} \frac{\partial \omega}{\partial(\ln \mu)} = -249$  THz. That is, if  $\mu$  were to increase by  $6 \times 10^{-14}$ , the frequency would decrease by 15 Hz. Because we are referencing our transition to iodine, we need to include any effect  $\mu$ -variation would have on that molecule. Most of the energy of the 531 nm transition goes to changing the I<sub>2</sub> molecule's electronic state from  $X \, {}^{1}\Sigma_{g}^{+}$  to  $B \, {}^{3}\Pi_{0u}^{+}$ . The particular iodine transition that appears to be closest to our  $O_{2}^{+}$  transition is between v'' = 0 in the X potential and v' = 32 in the B potential [40]. Using the molecular constants in ref. [40], we estimate this transition's sensitivity to be -36 THz. The net effect is to reduce our sensitivity by 10 % so that our measurement will have net sensitivity

Shift	Value	Estimate $(10^{-14})$
Systematics for $O_2^+$		
AC Stark shift (probe beam)	$\frac{\delta f}{f \times \Omega/(2\pi)} = -2.5 \times 10^{-15} \text{ Hz}^{-1}$	-25(1)
Stark shift (trap)	$\frac{\delta f}{f \times E^2} = -5.4 \times 10^{-24} \left(\frac{\rm V}{\rm m}\right)^{-2}$	-0.05(5)
Blackbody radiation	$-2.5 \times 10^{-18}$	-0.0003
First-order Doppler	0	0
Second-order Doppler	$\frac{\delta f}{f \times u_0^2} = -2.4 \times 10^{-16} \ \mu \mathrm{m}^{-2}$	-2(2)
Zeeman shift	0	0
Quadrupole shift	0	0
Systematics for $I_2$		
Pressure shift	$\frac{\delta f}{f \times P} = 5.3 \times 10^{-12} \text{ Pa}^{-1}$	300(2)
Light pressure shift	$\frac{\delta f}{f \times P} = 1.8 \times 10^{-12} \text{ mW}^{-1}$	200(1)

Table 2: Systematic effects. The last column gives estimates for experimental parameters described in the text.

-213 THz and a shift of  $6 \times 10^{-14}$  in  $\mu$  will lead to a shift in the transition of 12 Hz on 531.60 nm (6 Hz on 1063.20 nm), which is a fractional frequency of  $2 \times 10^{-14}$ . With the combination of the ULE cavity and iodine lock, this is achievable in precision.

In order to achieve that level of accuracy, we must evaluate systematic effects. Table 2 summarizes the leading systematics. The upshot is that the  $O_2^+$  system is largely immune from any perturbations at this precision and our main limitations will come from the I<sub>2</sub> reference.

We have chosen  $O_2^+$  for this measurement because it is nonpolar, so it is not surprising that electric-dipole-related shifts are small. By use of the same tabulated parameters [82] used to estimate the Rabi frequencies, we estimate the shifts from blackbody radiation, low-frequency Stark shifts (e.g. from the trapping fields), and AC Stark shifts (e.g. from the probe light). Ref. [19] calculates these shifts for other transitions in  $O_2^+$ , and we generally agree with its results. The probe beam's AC Stark shift is listed in the table as a function of Rabi frequency (assuming a Gaussian beam). For a 100 Hz Rabi frequency, we would have a shift of  $-2.5 \times 10^{-13}$ , which would require stabilizing the laser power at the 8% level. Typical commercial lasers and and amplifiers already meet this spec, but it can also be improved by feeding back to an AOM drive. We could reduce the shift further with lower intensity, reduce the uncertainty with better power stability, or suppress the shift with pulse sequences like the hyper- [114, 115] or auto-balanced [116] Ramsey methods, which are used on the electric-octupole (*E*3) clock transition in Yb<sup>+</sup>. We have the rf hardware in place to do such pulsing.

Any ion located off the rf null of our trap will experience Stark shifts from the trapping fields [117]. Our trap produces radial electric fields with curvature of order  $10^9 \text{ V/m}^2$ , which we can calibrate *in situ* using the motional frequencies of the trapped ions. To keep the shifts below  $2 \times 10^{14}$ , we would need to keep the ions within 60  $\mu$ m of the trap axis. As discussed below, we will likely confine them to within 10  $\mu$ m, which would have a 36-times smaller shift. At 300 K, we estimate the blackbody radiation shift to be negligible at  $-2.5 \times 10^{-18}$ .

First-order Doppler shifts are highly suppressed because the ions are trapped [118]. Any pos-

sible first-order shift can be monitored with counter-propagating probe beams [119]. Second-order Doppler shifts arise from finite temperature and micromotion [117]. At the 0.5 mK theoretical Doppler-cooling limit of Be<sup>+</sup>, the second-order Doppler shift would be  $-1.4 \times 10^{-18}$ . Even at significantly higher temperatures, this is negligible for our proposal. Excess micromotion, however, can produce significant shifts. Based on our current radial trapping parameters, we estimate that ions a distance  $u_0 = 10 \ \mu m$  off the rf null will have a shift of  $-2 \times 10^{-14}$ . Thus, we will run with long, thin crystals for the precision work.

The  ${}^{2}\Pi_{g}$  state is of Hund's case (a) and has two fine-structure manifolds. We choose the  $\Omega = 1/2$  states because they can suppress the quadrupole and Zeeman shifts. The quadrupole shift [120,121] arises in principle because of the non-zero quadrupole electric field in the ion trap. The shift scales as  $3M_{J}^{2} - J(J + 1)$  [19, 120, 121]. For states with J = 1/2, the quadrupole moment is exactly zero and so the shift is also exactly zero. The Zeeman shift is suppressed by 10<sup>3</sup> in the  $\Omega = 1/2$  state because the electron's orbital and spin magnetic moments largely cancel. There should be a residual shift of about 1 kHz/G (~ 10<sup>-3</sup> Bohr magnetons), but for transitions with  $\Delta M_{J} = 0$ , the net shift will also cancel. We have not yet estimated the quadratic Zeeman shift, but because the  $\Omega = 3/2$  fine-structure manifold has no J = 1/2 state, we expect it to be quite small.

Systematic shifts from iodine are discussed above. For the pressure shift, we would expect a pressure shift of a few kilohertz, but would calibrate it by varying the vapor pressure and extrapolating to zero pascals. During measurements, we would need cold-finger temperature stability around 0.06 K. Light-pressure shifts would also be calibrated, and would require 1% power stability.

### Long-term prospects

The  $O_2^+$  molecule and our chosen  $v = 0 \leftrightarrow 11$  transition have systematic effects that are favorable for several orders of magnitude improvement on the current-best limit of  $\dot{\mu}/\mu < 10^{-16}$  yr<sup>-1</sup> [30,31]. For a higher-precision experiment, the long lifetime of trapped ions would be key. It would allow greatly turning down the probe beam's intensity and thus AC Stark shift, which would also be suppressed with composite pulse sequences [114–116]. Fewer ions would be used such that they could all reside on the trap's rf null, which would suppress the trap Stark and second-order Doppler shifts. In order to increase the fraction of time devoted to probing the ions, a non-destructive quantum-logic detection technique [122, 123] would be used. The first intrinsic limit to be hit would be the blackbody shift at  $-2.5 \times 10^{-18}$ . For comparison, the Al<sup>+</sup> optical clock [101, 119], which has the smallest blackbody shift of currently used optical clocks, has room-temperature shift  $-8 \times 10^{-18}$  [124].

The other main change for a future measurement would be the replacement of the I<sub>2</sub> optical frequency reference with an optical atomic clock [27, 101–104]. The iodine reference is limited both by the cell (and thus pressure shifts) and the ~ 1 MHz natural linewidth of the transition. An optical atomic clock would have the added benefit that it is insensitive to variation in  $\mu$ . The clock comparison itself would require a frequency comb, which is now a standard (though expensive) technique.

### Timeline

We currently have in place the ion trap, beryllium cooling laser, and oxygen photoionization laser. We can load mixed crystals of  $Be^+$  and  $O_2^+$ .

This year (the last of our current grant), we are working on the beryllium photoionization laser, which will double as the  $O_2^+ | v' = 11 \rangle$  photodissociation laser. We are building and testing the time-of-flight mass spectrometer (ToF-MS) in a separate vacuum chamber. We are also working on a pulsed supersonic beam of  $O_2$ . Our proposed experiments do not rely on this beam working, but it would greatly enhance our  $O_2^+$  loading efficiency by increasing the density of molecules at the photoionization laser focus, decreasing the internal temperature of  $O_2$  and thus increasing the population in the low-J state we seek to ionize, and reducing the pressure of the experiment chamber.

In year one of this grant, we will acquire and assemble the 1063 nm master-laser system. We will demonstrate the narrow linewidth of the laser and lock it to iodine. We will also integrate our ToF-MS into our trap vacuum system, which will require a modification to our trap electronics to allow dumping the trap rapidly [92–97]. The PI anticipates being on sabbatical this entire year and will dedicate the majority of his time to this project.

In year two, we will observe the  $|X^2\Pi_{g,1/2}, v'' = 0, J'' = \frac{1}{2}\rangle \leftrightarrow |X^2\Pi_{g,1/2}, v' = 11, J' = \frac{1}{2}\rangle$ transition and measure its frequency in hertz relative to a calibrated iodine line [41]. We will investigate systematic shifts of the  $O_2^+$  and  $I_2$  systems.

In year three, we will measure our transition multiple times relative to the closest  $I_2$  line as a test of  $\mu$ -variation. Each  $O_2^+$  probe pulse will be time-stamped so the data can be analyzed for both drifts and oscillations in  $\mu$ . We will continue to investigate systematic shifts.

### 4 Broader Impacts

#### Impacts to science and the general public

Precision spectroscopy impacts fields beyond atomic, molecular, and optical physics, including chemistry, astronomy, astrophysics, high-energy particle physics, and quantum gravity. The techniques of trapped molecular ions can play an important role in quantum-state-controlled chemistry [125, 126], astrochemistry [127, 128], and the development of quantum information processors [129]. The optical transition used in this work has systematics favorable enough that it could one day be used as an optical clock [19, 27]. Indeed, if the tools can be developed to control and read out molecular states more efficiently, the additional levels in molecules make them more flexible than atoms for next-generation clocks [130, 131]. This proposal works on developing those techniques.

The general public retains an interest in many of the themes of this proposal, such as trapping atoms and molecules, control at the quantum level, quantum gravity, dark matter, and symmetries of nature. At the local level, the PI has worked to generate interest in these themes. I have given talks on my work to students and alumni. A student has built a "paperclip trap" (fig. 7) that demonstrates the principles of our atom/molecule trap by capturing a piece of dust in an alternating electric potential. The potential is just the 60 Hz power line transformed up to an amplitude of 6 kV [132], with hefty resistors as a safety current-limiter. A laser illuminates trapped particles such as dust or lycopodium spores. This semester, another student is building a mechanical model of our trap from a rotating saddle [133].

As part of this grant, we will install these demonstration pieces in the new science center at Amherst College that will open in summer 2018. We will place them on public display with information about trapped ions and their applications to precision measurements, timekeeping, and quantum information processing.

### **Training of students**

Undergraduate students will be crucial to the success of this research. Our lab has a good track record of interesting and exciting student projects and of students finding success after graduation. They have been involved in the preliminary planning that went into this proposal and will continue to work on the design, construction, data taking, analysis, and presentation of results. Current undergraduate Christian Pluchar is building the 235 nm photoioni-



Figure 7: Lycopodium spores levitated in a 6-kV, 60-Hz "paperclip trap".

zation/photodissociation laser for his senior honors thesis. Senior Alexander Frenett is conducting his thesis work making our ToF-MS as well as next-generation loading with a pulsed supersonic beam.

Student projects to be enabled by this support include: building an iodine modulation-transfer spectroscopy setup, building a temperature-stabilized vacuum enclosure for the ULE cavity, stabilizing the diode laser to the cavity and iodine, searching for and observing the resonance, and calibrating systematic effects in  $O_2^+$  and  $I_2$ . Along the way, there will be many small projects for newer students. Examples of such projects are building photodetectors given a design sensitivity and bandwidth or setting up a double-pass AOM.

Students will continue to have opportunities to present their work publicly. Summer students will have an on-campus poster session. Thesis students will present two public talks on their work. Several students will present at a national conference like DAMOP. They will co-author journal articles as the work progresses.

### Training of a postdoc

For a project of this scale, a postdoc will keep the momentum moving when the PI is called away for teaching or other duties. Funding for a postdoc does more than just advance the science, though. It will further the career of an accomplished scientist. As discussed more fully in my postdoctoral mentoring plan, the person hired for this work will join a community of scholars at Amherst. They will have the opportunity to lead an aspect of the research, to attend and present at conferences, and to mentor students in the lab.

# **References Cited**

- DeMille, D., Doyle, J. M. & Sushkov, A. O. Probing the frontiers of particle physics with tabletop-scale experiments. *Science* 357, 990–994 (2017).
- [2] Safronova, M. S., Budker, D., DeMille, D., Jackson Kimball, D. F., Derevianko, A. & Clark, C. W. Search for new physics with atoms and molecules (2017). ArXiv:1710.01833.
- [3] Salumbides, E. J., Koelemeij, J. C. J., Komasa, J., Pachucki, K., Eikema, K. S. E. & Ubachs, W. Bounds on fifth forces from precision measurements on molecules. *Phys. Rev. D* 87, 112008 (2013).
- [4] DeMille, D., Cahn, S. B., Murphree, D., Rahmlow, D. A. & Kozlov, M. G. Using molecules to measure nuclear spin-dependent parity violation. *Phys. Rev. Lett.* **100**, 023003 (2008).
- [5] Quack, M., Stohner, J. & Willeke, M. High-resolution spectroscopic studies and theory of parity violation in chiral molecules. Ann. Rev. Phys. Chem. 59, 741–769 (2008).
- [6] Baron, J., Campbell, W. C., DeMille, D., Doyle, J. M., Gabrielse, G., Gurevich, Y. V., Hess, P. W., Hutzler, N. R., Kirilov, E., Kozyryev, I., O'Leary, B. R., Panda, C. D., Parsons, M. F., Petrik, E. S., Spaun, B., Vutha, A. C., West, A. D. & ACME Collaboration. Order of magnitude smaller limit on the electric dipole moment of the electron. *Science* **343**, 269–272 (2014).
- [7] Cairncross, W. B., Gresh, D. N., Grau, M., Cossel, K. C., Roussy, T. S., Ni, Y., Zhou, Y., Ye, J. & Cornell, E. A. Precision measurement of the electron's electric dipole moment using trapped molecular ions. *Phys. Rev. Lett.* **119**, 153001 (2017).
- [8] Schiller, S. & Korobov, V. Tests of time independence of the electron and nuclear masses with ultracold molecules. *Phys. Rev. A* **71**, 032505 (2005).
- [9] Chin, C. & Flambaum, V. V. Enhanced sensitivity to fundamental constants in ultracold atomic and molecular systems near Feshbach resonances. *Phys. Rev. Lett.* **96**, 230801 (2006).
- [10] Flambaum, V. V. & Kozlov, M. G. Enhanced sensitivity to the time variation of the finestructure constant and  $m_p/m_e$  in diatomic molecules. *Phys. Rev. Lett.* **99**, 150801 (2007).
- [11] DeMille, D., Sainis, S., Sage, J., Bergeman, T., Kotochigova, S. & Tiesinga, E. Enhanced sensitivity to variation of  $m_e/m_p$  in molecular spectra. *Phys. Rev. Lett.* **100**, 043202 (2008).
- [12] Zelevinsky, T., Kotochigova, S. & Ye, J. Precision test of mass-ratio variations with latticeconfined ultracold molecules. *Phys. Rev. Lett.* **100**, 043201 (2008).
- [13] Carr, L. D., DeMille, D., Krems, R. V. & Ye, J. Cold and ultracold molecules: science, technology, and applications. New J. Phys. 11, 055049 (2009).
- [14] Chin, C., Flambaum, V. V. & Kozlov, M. G. Ultracold molecules: new probes on the variation of fundamental constants. New J. Phys. 11, 055048 (2009).

- [15] Kajita, M., Abe, M., Hada, M. & Moriwaki, Y. Estimated accuracies of pure XH<sup>+</sup> (X: even isotopes of group II atoms) vibrational transition frequencies: toward the test of the variance in m<sub>p</sub>/m<sub>e</sub>. J. Phys. B 44, 025402 (2011).
- [16] Jansen, P., Bethlem, H. L. & Ubachs, W. Perspective: Tipping the scales: Search for drifting constants from molecular spectra. J. Chem. Phys. 140, 010901 (2014).
- [17] Kajita, M., Gopakumar, G., Abe, M., Hada, M. & Keller, M. Test of  $m_p/m_e$  changes using vibrational transitions in N<sub>2</sub><sup>+</sup>. *Phys. Rev. A* **89**, 032509 (2014).
- [18] Hanneke, D., Carollo, R. A. & Lane, D. A. High sensitivity to variation in the proton-toelectron mass ratio in O<sub>2</sub><sup>+</sup>. *Phys. Rev. A* 94, 050101(R) (2016).
- [19] Kajita, M. Accuracy estimation for the <sup>16</sup>O<sub>2</sub><sup>+</sup> transition frequencies targeting the search for the variation in the proton-electron mass ratio. *Phys. Rev. A* **95**, 023418 (2017).
- [20] Bressel, U., Borodin, A., Shen, J., Hansen, M., Ernsting, I. & Schiller, S. Manipulation of individual hyperfine states in cold trapped molecular ions and application to HD<sup>+</sup> frequency metrology. *Phys. Rev. Lett.* **108**, 183003 (2012).
- [21] Germann, M., Tong, X. & Willitsch, S. Observation of electric-dipole-forbidden infrared transitions in cold molecular ions. *Nature Phys.* 10, 820–824 (2014).
- [22] Biesheuvel, J., Karr, J., Hilico, L., Eikema, K. S. E., Ubachs, W. & Koelemeij, J. C. J. Probing QED and fundamental constants through laser spectroscopy of vibrational transitions in HD<sup>+</sup>. *Nature Comms.* 7, 10385 (2016).
- [23] Häffner, H., Roos, C. F. & Blatt, R. Quantum computing with trapped ions. Phys. Rep. 469, 155–203 (2008).
- [24] Ozeri, R. The trapped-ion qubit tool box. Contemp. Phys. 52, 531–550 (2011).
- [25] Wineland, D. J. Nobel lecture: Superposition, entanglement, and raising Schrödinger's cat. *Rev. Mod. Phys.* 85, 1103–1114 (2013).
- [26] Heavner, T. P., Donley, E. A., Levi, F., Costanzo, G., Parker, T. E., Shirley, J. H., Ashby, N., Barlow, S. & Jefferts, S. R. First accuracy evaluation of NIST-F2. *Metrologia* 51, 174 (2014).
- [27] Ludlow, A. D., Boyd, M. M., Ye, J., Peik, E. & Schmidt, P. O. Optical atomic clocks. *Rev. Mod. Phys.* 87, 637–701 (2015).
- [28] Uzan, J.-P. The fundamental constants and their variation: observational and theoretical status. Rev. Mod. Phys. 75, 403–455 (2003).
- [29] Stadnik, Y. V. & Flambaum, V. V. Can dark matter induce cosmological evolution of the fundamental constants of nature? *Phys. Rev. Lett.* **115**, 201301 (2015).
- [30] Godun, R. M., Nisbet-Jones, P. B. R., Jones, J. M., King, S. A., Johnson, L. A. M., Margolis, H. S., Szymaniec, K., Lea, S. N., Bongs, K. & Gill, P. Frequency ratio of two optical clock transitions in <sup>171</sup>Yb<sup>+</sup> and constraints on the time variation of fundamental constants. *Phys. Rev. Lett.* **113**, 210801 (2014).

- [31] Huntemann, N., Lipphardt, B., Tamm, C., Gerginov, V., Weyers, S. & Peik, E. Improved limit on a temporal variation of  $m_p/m_e$  from comparisons of Yb<sup>+</sup> and Cs atomic clocks. *Phys. Rev. Lett.* **113**, 210802 (2014).
- [32] Flambaum, V. V. & Tedesco, A. F. Dependence of nuclear magnetic moments on quark masses and limits on temporal variation of fundamental constants from atomic clock experiments. *Phys. Rev. C* 73, 055501 (2006).
- [33] Shelkovnikov, A., Butcher, R. J., Chardonnet, C. & Amy-Klein, A. Stability of the protonto-electron mass ratio. *Phys. Rev. Lett.* **100**, 150801 (2008).
- [34] Kajita, M. Evaluation of variation in  $(m_p/m_e)$  from the frequency difference between the  ${}^{15}N_2^+$  and  ${}^{87}Sr$  transitions. Appl. Phys. B **122**, 203 (2016).
- [35] Stoehr, H., Mensing, F., Helmcke, J. & Sterr, U. Diode laser with 1 Hz linewidth. Opt. Lett. 31, 736–738 (2006).
- [36] Ludlow, A. D., Huang, X., Notcutt, M., Zanon-Willette, T., Foreman, S. M., Boyd, M. M., Blatt, S. & Ye, J. Compact, thermal-noise-limited optical cavity for diode laser stabilization at 1 × 10<sup>-15</sup>. Opt. Lett. **32**, 641–643 (2007).
- [37] Zhao, Y. N., Zhang, J., Stejskal, A., Liu, T., Elman, V., Lu, Z. H. & Wang, L. J. A vibrationinsensitive optical cavity and absolute determination of its ultrahigh stability. *Opt. Expr.* 17, 8970–8982 (2009).
- [38] Ye, J., Robertsson, L., Picard, S., Ma, L.-S. & Hall, J. L. Absolute frequency atlas of molecular I<sub>2</sub> lines at 532 nm. *IEEE T. on Instrum. Meas.* 48, 544–549 (1999).
- [39] Hong, F.-L., Ishikawa, J., Yoda, J., Ye, J., Ma, L.-S. & Hall, J. L. Frequency comparison of <sup>127</sup>I<sub>2</sub>-stabilized Nd:YAG lasers. *IEEE T. on Instrum. Meas.* 48, 532–536 (1999).
- [40] Gerstenkorn, S. & Luc, P. Atlas du Spectre d'Absorption de la Molecule d'Iode, 14 800–20 000 cm<sup>-1</sup> (CNRS, 1978).
- [41] Kobayashi, T., Akamatsu, D., Hosaka, K., Inaba, H., Okubo, S., Tanabe, T., Yasuda, M., Onae, A. & Hong, F.-L. Compact iodine-stabilized laser operating at 531 nm with stability at the 10<sup>-12</sup> level and using a coin-sized laser module. *Opt. Expr.* 23, 20749–20759 (2015).
- [42] Carollo, R. A., Lane, D. A., Kleiner, E. K., Kyaw, P. A., Teng, C. C., Ou, C. Y., Qiao, S. & Hanneke, D. Third-harmonic-generation of a diode laser for quantum control of beryllium ions. *Opt. Expr.* 25, 7220–7229 (2017).
- [43] Teng, C. C. Frequency Control and Stabilization of a Laser System. Undergraduate thesis, Amherst College (2013).
- [44] Kyaw, P. A. Constructing an Ultra-High Vacuum Chamber and a Radio Frequency Helical Resonator for Trapping Ions. Undergraduate thesis, Amherst College (2014).
- [45] Shi, J. Radiofrequency Synthesis System for Laser Modulation. Undergraduate thesis, Amherst College (2014).

- [46] Kleiner, E. K. Quantum Control of Be<sup>+</sup> Ions. Undergraduate thesis, Amherst College (2016).
- [47] Lane, D. A. Developing a Quantum Toolbox: Experiments with a Single-Atom Harmonic Oscillator and Prospects for Probing Molecular Ions. Undergraduate thesis, Amherst College (2017).
- [48] Herzberg, G. Molecular Spectra and Molecular Structure, Vol. I: Spectra of Diatomic Molecules (D. Van Nostrand Co., 1950).
- [49] Beloy, K., Kozlov, M. G., Borschevsky, A., Hauser, A. W., Flambaum, V. V. & Schwerdtfeger,
   P. Rotational spectrum of the molecular ion NH<sup>+</sup> as a probe for α and m<sub>e</sub>/m<sub>p</sub> variation.
   *Phys. Rev. A* 83, 062514 (2011).
- [50] Pašteka, L. F., Borschevsky, A., Flambaum, V. V. & Schwerdtfeger, P. Search for the variation of fundamental constants: Strong enhancements in X<sup>2</sup>Π cations of dihalogens and hydrogen halides. *Phys. Rev. A* **92**, 012103 (2015).
- [51] Song, Y., Evans, M., Ng, C. Y., Hsu, C.-W. & Jarvis, G. K. Rotationally resolved pulsed field ionization photoelectron bands of  $O_2^+(X\,^2\Pi_{1/2,3/2g}, v^+ = 0 38)$  in the energy range of 12.05 18.15 eV. J. Chem. Phys. **111**, 1905–1916 (1999).
- [52] Song, Y., Evans, M., Ng, C. Y., Hsu, C.-W. & Jarvis, G. K. Rotationally resolved pulsed-field ionization photoelectron bands of  $O_2^+(A^2\Pi_u, v^+ = 0 12)$  in the energy range of 17.0 18.2 eV. J. Chem. Phys. **112**, 1271–1278 (2000).
- [53] Song, Y., Evans, M., Ng, C. Y., Hsu, C.-W. & Jarvis, G. K. Rotationally resolved pulsed field ionization photoelectron bands of  $O_2^+(a\,^4\Pi_u, v^+ = 0 18)$  in the energy range of 16.0 18.0 eV. J. Chem. Phys. **112**, 1306–1315 (2000).
- [54] Kajita, M.  $N_2^+$  quadrupole transitions with small Zeeman shift. *Phys. Rev. A* **92**, 043423 (2015).
- [55] Krupenie, P. H. The spectrum of molecular oxygen. J. Phys. Chem. Ref. Data 1, 423–534 (1972).
- [56] Cosby, P. C., Ozenne, J.-B., Moseley, J. T. & Albritton, D. L. High-resolution photofragment spectroscopy of the  $O_2^+$   $b^4 \Sigma_g^-(v'=3,4,5) \leftarrow a^4 \Pi_u(v'=3,4,5)$  first negative system using coaxial dye-laser and velocity-tuned ion beams. J. Mol. Spec. **79**, 203–235 (1980).
- [57] Hansen, J. C., Moseley, J. T. & Cosby, P. C. High-resolution photofragment spectroscopy of the  $O_2^+ b^4 \Sigma_g^- (v' = 5 8) \leftarrow a^4 \Pi_u (v'' = 6 9)$  first negative system. J. Mol. Spec. **98**, 48–63 (1983).
- [58] Coxon, J. A. & Haley, M. P. Rotational analysis of the  $A^2\Pi_u \to X^2\Pi_g$  second negative band system of  ${}^{16}O_2^+$ . J. Mol. Spec. 108, 119–136 (1984).
- [59] Kong, W. & Hepburn, J. W. Rotationally resolved threshold photoelectron spectroscopy of O<sub>2</sub> using coherent XUV: formation of vibrationally excited ions in the Franck–Condon gap. *Can. J. Phys.* **72**, 1284–1293 (1994).

- [60] Kong, W. & Hepburn, J. W. PFI-ZEKE spectroscopy using coherent vacuum UV:  $O_2^+(a \, {}^4\Pi_u) \leftarrow O_2(X \, {}^3\Sigma_a^-)$ . Int. J. Mass Spectrom. Ion Proc. **159**, 27–35 (1996).
- [61] Fedorov, D. G., Evans, M., Song, Y., Gordon, M. S. & Ng, C. Y. An experimental and theoretical study of the spin-orbit interaction for CO<sup>+</sup> ( $A^2\Pi_{3/2,1/2}, v^+ = 0 41$ ) and  $O_2^+(X\,^2\Pi_{3/2,1/2q}, v^+ = 0 38)$ . J. Chem. Phys. **111**, 6413–6421 (1999).
- [62] Fedorov, D. G., Gordon, M. S., Song, Y. & Ng, C. Y. Theoretical study of spin-orbit coupling constants for  $O_2^+(A^2\Pi_{3/2,1/2u}, v^+ = 0 17 \text{ and } a^4\Pi_{5/2,3/2,1/2,-1/2u}, v^+ = 0 25)$ . J. Chem. Phys. **115**, 7393–7400 (2001).
- [63] Zhang, X., Shi, D., Sun, J. & Zhu, Z. MRCI study of spectroscopic and molecular properties of  $X^2\Pi_g$ ,  $a^4\Pi_u$ ,  $A^2\Pi_u$ ,  $b^4\Sigma_g^-$ ,  $D^2\Delta_g$  and  $B^2\Sigma_g^-$  electronic states of  $O_2^+$  ion. *Mol. Phys.* **109**, 1627–1638 (2011).
- [64] Magrakvelidze, M., Aikens, C. M. & Thumm, U. Dissociation dynamics of diatomic molecules in intense laser fields: A scheme for the selection of relevant adiabatic potential curves. *Phys. Rev. A* 86, 023402 (2012).
- [65] Liu, H., Shi, D., Sun, J. & Zhu, Z. Accurate theoretical investigations of the 20 A-S and 58  $\Omega$  states of  $O_2^+$  cation including spin-orbit coupling effect. *Mol. Phys.* **113**, 120–136 (2015).
- [66] Kim, D.-S., Zhou, H.-L., Manson, S. T. & Tayal, S. S. Photoionization of the excited  $1s^22s2p^{1,3}P^o$  states of atomic beryllium. *Phys. Rev. A* **64**, 042713 (2001).
- [67] Lo, H.-Y., Alonso, J., Kienzler, D., Keitch, B. C., de Clercq, L. E., Negnevitsky, V. & Home, J. P. All-solid-state continuous-wave laser systems for ionization, cooling and quantum state manipulation of beryllium ions. *Appl. Phys. B* **114**, 17–25 (2014).
- [68] Lin, Y. Quantum entanglement generation in trapped ions using coherent and dissipative methods. Ph.D. thesis, University of Colorado (2015).
- [69] Bowler, R. Coherent Ion Transport in a Multi-electrode Trap Array. Ph.D. thesis, University of Colorado (2015).
- [70] Tan, T. R. *High-Fidelity Entangling Gates with Trapped-Ions*. Ph.D. thesis, University of Colorado (2016).
- [71] Blakestad, R. B. Transport of Trapped-Ion Qubits within a Scalable Quantum Processor. Ph.D. thesis, University of Colorado (2010).
- [72] Ogorzalek Loo, R., Marinelli, W. J., Houston, P. L., Arepalli, S., Wiesenfeld, J. R. & Field, R. W. Multiphoton ionization of O<sub>2</sub>  $X^{3}\Sigma_{g}^{-}$ ,  $a^{1}\Delta_{g}$ , and  $b^{1}\Sigma_{g}^{+}$  via the two-photon resonant  $ns\sigma_{g}$ ,  $nd\sigma_{g}$ , and  $nd\pi_{g}$  Rydberg levels. J. Chem. Phys. **91**, 5185–5200 (1989).
- [73] Sur, A., Friedman, R. S. & Miller, P. J. Rotational dependence of the Rydberg-valence interactions in the  ${}^{1}\Pi_{q}$  states of molecular oxygen. J. Chem. Phys. **94**, 1705–1711 (1991).
- [74] Dochain, A. & Urbain, X. Production of a rovibrationally selected O<sub>2</sub><sup>+</sup> beam for dissociative recombination studies. *EPJ Web of Conferences* 84, 05001 (2015).

- [75] Xie, J. & Zare, R. N. Selection rules for the photoionization of diatomic molecules. J. Chem. Phys. 93, 3033–3038 (1990).
- [76] Germann, M. & Willitsch, S. Fine- and hyperfine-structure effects in molecular photoionization. I. general theory and direct photoionization. J. Chem. Phys. 145, 044314 (2016).
- [77] Miyake, A., Kost-Smith, L. E., Finkelstein, N. D., Pollock, S. J., Cohen, G. L. & Ito, T. A. Reducing the gender achievement gap in college science: A classroom study of values affirmation. *Science* **330**, 1234–1237 (2010).
- [78] Khanyile, N. B., Shu, G. & Brown, K. R. Observation of vibrational overtones by singlemolecule resonant photodissociation. *Nature Comm.* 6, 7825 (2015).
- [79] Parthey, C. G., Matveev, A., Alnis, J., Bernhardt, B., Beyer, A., Holzwarth, R., Maistrou, A., Pohl, R., Predehl, K., Udem, T., Wilken, T., Kolachevsky, N., Abgrall, M., Rovera, D., Salomon, C., Laurent, P. & Hänsch, T. W. Improved measurement of the hydrogen 1s-2s transition frequency. *Phys. Rev. Lett.* **107**, 203001 (2011).
- [80] Matveev, A., Parthey, C. G., Predehl, K., Alnis, J., Beyer, A., Holzwarth, R., Udem, T., Wilken, T., Kolachevsky, N., Abgrall, M., Rovera, D., Salomon, C., Laurent, P., Grosche, G., Terra, O., Legero, T., Schnatz, H., Weyers, S., Altschul, B. & Hänsch, T. W. Precision measurement of the hydrogen 1s-2s frequency via a 920-km fiber link. *Phys. Rev. Lett.* 110, 230801 (2013).
- [81] Schunk, R. W. & Nagy, A. F. Ionospheres of the terrestrial planets. Rev. Geophys. Space Phys. 18, 813–852 (1980).
- [82] Gilmore, F. R., Laher, R. R. & Espy, P. J. Franck-Condon factors, r-centroids, electronic transition moments, and Einstein coefficients for many nitrogen and oxygen band systems. J. Phys. Chem. Ref. Data 21, 1005–1107 (1992).
- [83] Włodarczyk, P., Pustelny, S., Budker, D. & Lipiński, M. Multi-channel data acquisition system with absolute time synchronization. *Nuc. Inst. Meth. Phys. Res. A* 763, 150–154 (2014).
- [84] Schlemmer, S., Kuhn, T., Lescop, E. & Gerlich, D. Laser excited N<sub>2</sub><sup>+</sup> in a 22-pole ion trap: Experimental studies of rotational relaxation processes. *Int. J. Mass Spectrom.* 185, 589–602 (1999).
- [85] Tong, X., Winney, A. H. & Willitsch, S. Sympathetic cooling of molecular ions in selected rotational and vibrational states produced by threshold photoionization. *Phys. Rev. Lett.* 105, 143001 (2010).
- [86] IzumiWaki, T. Cooling and mass-analysis of molecules using laser-cooled atoms. Jpn. J. Appl. Phys. 35, L1134–L1137 (1996).
- [87] Roth, B., Koelemeij, J. C. J., Daerr, H. & Schiller, S. Rovibrational spectroscopy of trapped molecular hydrogen ions at millikelvin temperatures. *Phys. Rev. A* 74, 040501 (2006).

- [88] Fröhlich, U., Roth, B. & Schiller, S. Ellipsoidal Coulomb crystals in a linear radio-frequency trap. Phys. Plasmas 12, 073506 (2005).
- [89] Roth, B., Ostendorf, A., Wenz, H. & Schiller, S. Production of large molecular ion crystals via sympathetic cooling by laser-cooled Ba<sup>+</sup>. J. Phys. B 38, 3673–3685 (2005).
- [90] Ostendorf, A., Zhang, C. B., Wilson, M. A., Offenberg, D., Roth, B. & Schiller, S. Sympathetic cooling of complex molecular ions to millikelvin temperatures. *Phys. Rev. Lett.* 97, 243005 (2006).
- [91] Wiley, W. C. & McLaren, I. H. Time-of-flight mass spectrometer with improved resolution. *Rev. Sci. Instrum.* 26, 1150–1157 (1955).
- [92] Schowalter, S. J., Chen, K., Rellergert, W. G., Sullivan, S. T. & Hudson, E. R. An integrated ion trap and time-of-flight mass spectrometer for chemical and photo- reaction dynamics studies. *Rev. Sci. Instrum.* 83, 043103 (2012).
- [93] Seck, C. M., Hohenstein, E. G., Lien, C.-Y., Stollenwerk, P. R. & Odom, B. C. Rotational state analysis of AlH<sup>+</sup> by two-photon dissociation. J. Mol. Spec. **300**, 108–111 (2014).
- [94] Deb, N., Pollum, L. L., Smith, A. D., Keller, M., Rennick, C. J., Heazlewood, B. R. & Softley, T. P. Coulomb crystal mass spectrometry in a digital ion trap. *Phys. Rev. A* 91, 033408 (2015).
- [95] Meyer, K. A. E., Pollum, L. L., Petralia, L. S., Tauschinsky, A., Rennick, C. J., Softley, T. P. & Heazlewood, B. R. Ejection of Coulomb crystals from a linear Paul ion trap for ion-molecule reaction studies. J. Chem. Phys. A 119, 12449–12456 (2015).
- [96] Schneider, C., Schowalter, S. J., Yu, P. & Hudson, E. R. Electronics of an ion trap with integrated time-of-flight mass spectrometer. *International Journal of Mass Spectrometry* **394**, 1–8 (2016).
- [97] Schmid, P. C., Greenberg, J., Miller, M. I., Loeffler, K. & Lewandowski, H. J. High resolution ion trap time-of-flight mass spectrometer for cold trapped ion experiments (2017). ArXiv:1707.07036.
- [98] Heine, T., Heidemann, R. & Toptica Photonics AG. Tunable diode laser system with external resonator (2011). US Patent 7970024.
- [99] Young, B. C., Cruz, F. C., Itano, W. M. & Bergquist, J. C. Visible lasers with subhertz linewidths. *Phys. Rev. Lett.* 82, 3799–3802 (1999).
- [100] Itano, W. M., Bergquist, J. C., Bollinger, J. J., Gilligan, J. M., Heinzen, D. J., Moore, F. L., Raizen, M. G. & Wineland, D. J. Quantum projection noise: Population fluctuations in two-level systems. *Phys. Rev. A* 47, 3554–3570 (1993).
- [101] Chou, C. W., Hume, D. B., Koelemeij, J. C. J., Wineland, D. J. & Rosenband, T. Frequency comparison of two high-accuracy Al<sup>+</sup> optical clocks. *Phys. Rev. Lett.* **104**, 070802 (2010).

- [102] Nicholson, T. L., Campbell, S. L., Hutson, R. B., Marti, G. E., Bloom, B. J., McNally, R. L., Zhang, W., Barrett, M. D., Safronova, M. S., Strouse, G. F., Tew, W. L. & Ye, J. Systematic evaluation of an atomic clock at 2 × 10<sup>-18</sup> total uncertainty. *Nature Comm.* 6, 6896 (2015).
- [103] Ushijima, I., Takamoto, M., Das, M., Ohkubo, T. & Katori, H. Cryogenic optical lattice clocks. *Nature Photon.* 9, 185–189 (2015).
- [104] Huntemann, N., Sanner, C., Lipphardt, B., Tamm, C. & Peik, E. Single-ion atomic clock with  $3 \times 10^{-18}$  systematic uncertainty. *Phys. Rev. Lett.* **116**, 063001 (2016).
- [105] Ye, J. & Cundiff, S. T. (eds.) Femtosecond Optical Frequency Comb: Principle, Operation, and Applications (Kluwer Academic Publishers/Springer, 2005).
- [106] URL https://www.ntt-electronics.com/en/products/photonics/conversion\_module. html. NTT (formerly NEL) Electronics spec sheet.
- [107] Sakai, K., Koyata, Y., Shimada, N., Shibata, K., Hanamaki, Y., Itakura, S., Yagi, T. & Hirano, Y. Master-oscillator power-amplifier scheme for efficient green-light generation in a planar MgO:PPLN waveguide. *Opt. Lett.* **33**, 431–433 (2008).
- [108] Lévèque, T., Antoni-Micollier, L., Faure, B. & Berthon, J. A laser setup for rubidium cooling dedicated to space applications. *Appl. Phys. B* **116**, 997–1004 (2014).
- [109] Ye, J., Ma, L. S. & Hall, J. L. Molecular iodine clock. *Phys. Rev. Lett.* 87, 270801 (2001).
- [110] Raj, R. K., Bloch, D., Snyder, J. J., Camy, G. & Ducloy, M. High-frequency optically heterodyned saturation spectroscopy via resonant degenerate four-wave mixing. *Phys. Rev. Lett.* 44, 1251–1254 (1980).
- [111] Shirley, J. H. Modulation transfer processes in optical heterodyne saturation spectroscopy. Opt. Lett. 7, 537–539 (1982).
- [112] Hall, J. L., Ma, L.-S., Taubman, M., Tiemann, B., Hong, F.-L., Pfister, O. & Ye, J. Stabilization and frequency measurement of the I<sub>2</sub>-stabilized Nd:YAG laser. *IEEE T. on Instrum. Meas.* 48, 583–586 (1999).
- [113] Gillespie, L. J. & Fraser, L. H. D. The normal vapor pressure of crystalline iodine. J. Am. Chem. Soc. 58, 2260–2263 (1936).
- [114] Yudin, V. I., Taichenachev, A. V., Oates, C. W., Barber, Z. W., Lemke, N. D., Ludlow, A. D., Sterr, U., Lisdat, C. & Riehle, F. Hyper-Ramsey spectroscopy of optical clock transitions. *Phys. Rev. A* 82, 011804 (2010).
- [115] Huntemann, N., Lipphardt, B., Okhapkin, M., Tamm, C., Peik, E., Taichenachev, A. V. & Yudin, V. I. Generalized Ramsey excitation scheme with suppressed light shift. *Phys. Rev. Lett.* 109, 213002 (2012).
- [116] Sanner, C., Huntemann, N., Lange, R., Tamm, C. & Peik, E. Auto-balanced Ramsey spectroscopy (2017). ArXiv:1707.02630.

- [117] Berkeland, D. J., Miller, J. D., Bergquist, J. C., Itano, W. M. & Wineland, D. J. Minimization of ion micromotion in a Paul trap. J. Appl. Phys. 83, 5025–5033 (1998).
- [118] Dicke, R. H. The effect of collisions upon the Doppler width of spectral lines. Phys. Rev. 89, 472–473 (1953).
- [119] Rosenband, T., Hume, D. B., Schmidt, P. O., Chou, C. W., Brusch, A., Lorini, L., Oskay, W. H., Drullinger, R. E., Fortier, T. M., Stalnaker, J. E., Diddams, S. A., Swann, W. C., Newbury, N. R., Itano, W. M., Wineland, D. J. & Bergquist, J. C. Frequency ratio of Al<sup>+</sup> and Hg<sup>+</sup> single-ion optical clocks; metrology at the 17th decimal place. *Science* **319**, 1808–1812 (2008).
- [120] Itano, W. M. External-field shifts of the <sup>199</sup>Hg<sup>+</sup> optical frequency standard. J. Res. Natl. Inst. Stand. Tech. 105, 829–837 (2000).
- [121] Bakalov, D. & Schiller, S. The electric quadrupole moment of molecular hydrogen ions and their potential for a molecular ion clock. *Appl. Phys. B* **114**, 213–230 (2014).
- [122] Schmidt, P. O., Rosenband, T., Langer, C., Itano, W. M., Bergquist, J. C. & Wineland, D. J. Spectroscopy using quantum logic. *Science* **309**, 749–752 (2005).
- [123] Wolf, F., Wan, Y., Heip, J. C., Gerbert, F., Shi, C. & Schmidt, P. O. Non-destructive state detection for quantum logic spectroscopy of molecular ions. *Nature* 530, 457–460 (2016).
- [124] Rosenband, T., Itano, W. M., Schmidt, P. O., Hume, D. B., Koelemeij, J. C. J., Bergquist, J. C. & Wineland, D. J. Blackbody radiation shift of the  ${}^{27}\text{Al}^+$   ${}^{1}\text{S}_0 \rightarrow {}^{3}\text{P}_0$  transition (2006). ArXiv:physics/0611125.
- [125] Willitsch, S., Bell, M. T., Gingell, A. D. & Softley, T. P. Chemical applications of laser- and sympathetically-cooled ions in ion traps. *Phys. Chem. Chem. Phys.* 10, 7200–7210 (2008).
- [126] Krems, R. V. Cold controlled chemistry. *Phys. Chem. Chem. Phys.* **10**, 4079–4092 (2008).
- [127] Gerlich, D. & Smith, M. Laboratory astrochemistry: studying molecules under inter- and circumstellar conditions. *Phys. Scr.* 73, C25 (2006).
- [128] Millar, T. J. Astrochemistry. Plasma Sources Sci. Technol. 24, 043001 (2015).
- [129] Schuster, D. I., Bishop, L. S., Chuang, I. L., DeMille, D. & Schoelkopf, R. J. Cavity QED in a molecular ion trap. *Phys. Rev. A* 83, 012311 (2011).
- [130] Karr, J.-P.  $H_2^+$  and  $HD^+$ : Candidates for a molecular clock. J. Mol. Spec. **300**, 37–43 (2014).
- [131] Schiller, S., Bakalov, D. & Korobov, V. I. Simplest molecules as candidates for precise optical clocks. *Phys. Rev. Lett.* **113**, 023004 (2014).
- [132] Winter, H. & Ortjohann, H. W. Simple demonstration of storing macroscopic particles in a "Paul trap". Am. J. Phys. 59, 807–813 (1991).
- [133] Fan, W., Du, L., Wang, S. & Zhou, H. Confining rigid balls by mimicking quadrupole ion trapping. Am. J. Phys. 85, 821–829 (2017).

## **Biographical Sketch: David A. Hanneke**

## **Professional Preparation**

Institution	<u>Major</u>	Degree	Year
Case Western Reserve University	Physics	B.S.	2001
Harvard University	Physics	A.M.	2003
Harvard University	Physics	Ph.D.	2008
National Institute of Standards and Technology		(Postdoc)	2008-2010
University of Colorado at Boulder & NIST		(Postdoc)	2010-2011

## Appointments

Assistant Professor of Physics, Amherst College, 2011-present

## Closely related publications (\* indicates undergraduate)

Third-harmonic-generation of a diode laser for quantum control of beryllium ions R. A. Carollo, D. A. Lane\*, E. K. Kleiner\*, P. A. Kyaw\*, C. C. Teng\*, C. Y. Ou\*, S. Qiao\*, and D. Hanneke Optics Express 25, 7220–7229 (2017) DOI: 10.1364/OE.25.007220 High sensitivity to variation in the proton-to-electron mass ratio in  $O_2^+$ D. Hanneke, R. A. Carollo, and D. A. Lane\* *Physical Review A* 94, 050101(R) (2016) DOI: 10.1103/PhysRevA.94.050101 Cavity control of a single-electron quantum cyclotron: Measuring the electron magnetic moment D. Hanneke, S. Fogwell Hoogerheide, and G. Gabrielse Physical Review A 83, 052122 (2011) DOI: 10.1103/PhysRevA.83.052122 New Measurement of the Electron Magnetic Moment and the Fine Structure Constant D. Hanneke, S. Fogwell, and G. Gabrielse Physical Review Letters 100, 120801 (2008) DOI: 10.1103/PhysRevLett.100.120801 Realization of a programmable two-qubit quantum processor D. Hanneke, J. P. Home, J. D. Jost, J. M. Amini, D. Leibfried & D. J. Wineland *Nature Physics* **6**, 13–16 (2010) DOI: 10.1038/NPHYS1453

## Other significant publications

Coherent Diabatic Ion Transport and Separation in a Multi-Zone Trap Array
R. Bowler, J. Gaebler, Y. Lin, T. R. Tan, D. Hanneke, J. D. Jost, J. P. Home,
D. Leibfried, D. J. Wineland
Physical Review Letters 109, 080502 (2012)
DOI: 10.1103/PhysRevLett.109.080502

Normal modes of trapped ions in the presence of anharmonic trap potentials J. P. Home, D. Hanneke, J. D. Jost, D. Leibfried, D. J. Wineland *New Journal of Physics* **13**, 073026 (2011) DOI: 10.1088/1367-2630/13/7/073026 Complete Methods Set for Scalable Ion Trap Quantum Information Processing J. P. Home, D. Hanneke, J. D. Jost, J. M. Amini, D. Leibfried, D. J. Wineland Science **325**, 1227–1230 (2009) DOI: 10.1126/science.1177077 *Entangled Mechanical Oscillators* J. D. Jost, J. P. Home, J. M. Amini, D. Hanneke, R. Ozeri, C. Langer, J. J. Bollinger, D. Leibfried, and D. J. Wineland Nature 459, 683-685 (2009) DOI: 10.1038/nature08006 Single-Particle Self-Excited Oscillator B. D'Urso, R. Van Handel, B. Odom, D. Hanneke, and G. Gabrielse *Physical Review Letters* **94**, 113002 (2005) DOI: 10.1103/PhysRevLett.94.113002

# **Synergistic Activities**

Member-at-Large on Executive Committee of APS's Topical Group on Precision Measurements & Fundamental Constants (2015–2018)

- Launched targeted recruitment effort at conferences
- Grew membership more than 10 % to over 500

Referee for Physical Review Letters, A, X, Review of Scientific Instruments, Foundations of Physics

Member of the Curriculum Committee for Amherst College's Department of Physics & Astronomy

- Revised the Physics major requirements
- Emphasized continued high-quality instruction, flexible paths through major, and accessibility to a diverse student body
- Revised lab instruction and added a new course with labs
- Wrote the department's first *Student Handbook*

Advisor to the Amherst College Electronics Club

• Supported numerous projects, including a high-altitude balloon that took video up to 31 km and back

Delivered the Michelson Postdoctoral Prize Lectures, Case Western Reserve University, 2010

# **Budget Justification**

## A.1. Senior Personnel

I request two-months of summer salary per year to support my work on this project. I have included a 4% cost-of-living adjustment.

## **B.** Other Personnel

## **B.1.** Postdoctoral Scholars

I request support for a postdoc for two years, split over three years as 0.5 yr, 1 yr, 0.5 yr. A postdoc will be important in maintaining progress during the academic term and providing continuity as students graduate. The postdoc's role is more fully discussed in the *Postdoctoral Researcher Mentoring Plan*. I have included an approximately 4% cost-of-living adjustment.

## **B.4.** Undergraduate Students

I include funds for summer support for one student for ten weeks per year. Student summer costs are \$\_\_\_\_ an hour for 40 hours per week.

# C. Fringe Benefits

The faculty, postdoctoral, and student salaries have respective benefits rates of 19.0%, 29.0%, and 0%.

# D. Equipment

The **year-one** equipment budget will allow for acquiring and assembling the 1063 nm optical source. The budget breaks down as follows:

- 1. Master diode laser at 1063 nm (e.g. Toptica DLC DL Pro): \$\_\_\_\_
- 2. Linewidth-narrowing cavity
  - High-finesse ULE cavity: \$\_\_\_\_
  - Ion vacuum pumps for enclosure: \$\_\_\_\_
  - Electronics for stabilizing the laser (e.g. Toptica FALC and PDD modules with chassis):\$\_\_\_\_
- 3. Fiber-coupled PPLN waveguide doubler: \$\_\_\_\_

The ULE cavity will require a vacuum enclosure, but we have the capabilities to make that inhouse to save considerable expense. The waveguide doubler creates the 531.6 nm light for locking to iodine.

The **year two** equipment budget will purchase the high-power fiber amplifier that will allow driving the two-photon transition.

1. Ytterbium-doped fiber amplifier (10 W): \$\_\_\_\_\_

These prices were determined from formal quotations from leading companies (Toptica Photonics, Stable Laser Systems, NEL/NTT Electronics, HCP Photonics, IPG Photonics).

# E.1. Domestic Travel

Conferences are an important part of the scientific endeavor. I request funds to allow travel to a conference (e.g. DAMOP) for the postdoc, at least one student, and myself.

# G. Other direct costs

## G.1. Materials and Supplies

I include \$\_\_\_\_\_ a year for the first two years and \$\_\_\_\_\_ in year three to cover construction and improvements to the apparatus. The first two years will require a considerable amount of construction, including the ULE cavity's vacuum enclosure and the iodine modulation-transfer spectroscopy and temperature-stabilization setup. Like most tabletop atomic physics experiments, ours is largely self-built. While we will require some funds for materials and consumables, most of the funds will go to two categories: optics and electronics.

- *Optics*: Our optics needs include acousto- and electro-optic modulators, safety equipment, and general optics like mirrors, lenses, waveplates, polarizers, and fiber optics. We may need to replace a laser diode or tapered amplifier on our 313 nm system.
- *Electronics*: Our electronics needs revolve around thermal stabilization (of cavities, vapor cells, and lasers), laser control (current controllers and servolocks), computer control (ADC/DAC/DAQ boards, microcontrollers, oscilloscopes), and radiofrequency generation (signal generators, direct-digital synthesis (DDS) boards, mixers, splitters, amplifiers).

## G.2. Publication Costs

I include funds for dissemination of our results. The requested amounts are in line with the current publication charge at *Physical Review Letters* (\$765). We will likely also publish details about our optical system in one of the journals of the OSA (*Optics Letters* fee \$125/page).

## G.6. Other

I include funds for housing an undergraduate student for 10 weeks during the summer. The housing fee is \$125 per week.

## I. Indirect Costs

All personnel costs (sections A, B, and C) are subject to the indirect cost rate of 55.5%.

# **Current and Pending Support**

(See PAPPG Section II.C.2.h for guidance on information to include on this form.) The following information should be provided for each investigator and other senior personnel. Failure to provide this information may delay consideration of this proposal. Other agencies (including NSF) to which this proposal has been/will be submitted. Investigator: David Hanneke Support: Current □ Pending □ Submission Planned in Near Future □ \*Transfer of Support CAREER: Fundamental Physics through Precision Measurements Project/Proposal Title: of Trapped Charged Particles NSF Source of Support: Total Award Amount: \$ 600,000 Total Award Period Covered: 06/01/13 - 05/31/18 Amherst College Location of Project: Person-Months Per Year Committed to the Project. Cal:0.00 Acad: 0.00 Sumr: 2.00 Current ☑ Pending □ Submission Planned in Near Future □ \*Transfer of Support Support: Project/Proposal Title: RUI: Driving Forbidden Vibrational Overtones in Trapped Molecular lons (This proposal) NSF Source of Support: 514,119 Total Award Period Covered: Total Award Amount: \$ 07/01/18 - 06/30/21 Location of Project: Amherst College Person-Months Per Year Committed to the Project. Cal:0.00 Acad: 0.00 Sumr: 2.00 Support: Current □ Pending □ Submission Planned in Near Future □ \*Transfer of Support Project/Proposal Title: Source of Support: Total Award Amount: \$ **Total Award Period Covered:** Location of Project: Person-Months Per Year Committed to the Project. Cal: Acad: Sumr: Submission Planned in Near Future Support: □ Current Pending □ \*Transfer of Support Project/Proposal Title: Source of Support: Total Award Amount: \$ **Total Award Period Covered:** Location of Project: Person-Months Per Year Committed to the Project. Cal: Acad: Sumr: Support: □ Current Pending □ Submission Planned in Near Future □ \*Transfer of Support Project/Proposal Title: Source of Support: Total Award Amount: \$ **Total Award Period Covered:** Location of Project: Person-Months Per Year Committed to the Project. Acad: Summ: Cal: \*If this project has previously been funded by another agency, please list and furnish information for immediately preceding funding period.

## Facilities, Equipment and Other Resources

At the start of this grant, Amherst College will have just commissioned a new 250,000 square-foot science center with state-of-the-art laboratories and shops. Within this new space, Amherst College will provide without charge many facilities, including personnel, in support of this research. These include

- Laboratory space,
- Staffed machine shop,
- Staffed electronics shop,
- Extensive library with many journals available online,
- Utilities (electricity, water, deionized water, processed chilled water, LN<sub>2</sub>),
- Computing facilities (internet access, a computer cluster, software such as Mathematica, Matlab, Solidworks, and LabView),
- A department laboratory technician, and
- Secretarial support.

We may also draw on the library facilities and other resources of the Five College Consortium (Amherst, Hampshire, Mount Holyoke, and Smith Colleges as well as the University of Massachusetts).

Amherst College provides funding for some students over the summer and occasionally during the academic term. It provides a small amount to assist student travel to conferences. We have also made use of the DAMOP student travel grants.

The Physics & Astronomy Department at Amherst College will occupy parts of the first two floors of the new science center. The second floor will house a dedicated physics classroom, six teaching laboratories, and storage space for teaching equipment. The first floor houses the physics research labs and the college electronics and machine shops. The machine shop is 2,700 square feet and is fully equipped with lathes, milling machines, bandsaws, sheet metal equipment, grinders, and welding equipment. We have a three-axis CNC mill with tool-changer that we have had great success using on intricate projects such as our trap electrodes. Our machinist, Jim Kubasek, has extensive experience with precision machining, but also with educating. Twice a year, he teaches three-week machine shop classes to students. Upon completion, they have access to a 500+ squarefoot faculty/student shop, which is also equipped with lathes, milling machines, and other tools.

The Physics & Astronomy Department hosts five experimental research programs. While the physics goals are diverse, the techniques overlap enough for sharing of some common equipment. Four of the groups make extensive use of lasers and optics, a different four produce vacuum or ultrahigh vacuum, and four require precision radio frequency and microwaves. We routinely share equipment including leak detectors, a dry pump-out station with turbomolecular pump, a bake-out setup for ultrahigh vacuum chambers, and radiofrequency test and measurement equipment including a spectrum analyzer and vector network analyzer.

The PI's laboratory consists of approximately 1,000 square feet of space. I have been involved in the design process from the beginning, and the laboratory is being constructed based on the needs of my research program. This space is subdivided into two roughly equal size rooms: one for the main experiment and all laser radiation and one for prep work. The lab temperature is designed to be stable within approximately 0.1 °C under constant heat load. The lab is located on the ground floor of the building in a corner and designed to be low-vibration (VC-D spec). The ceilings are 13' high and have embedded anchors capable of holding significant weight. They will be used for suspending platforms with utilities and electronics above the laser tables. In addition to standard laboratory equipment and supplies, the following more specialized equipment is available.

### Ion trap and control accessories

- Ion trap (linear rf trap with segmented electrodes)
- rf source (oscillator, power amplifier, home-made helical resonator)
- DC source (NI PXI-6723 analog waveform generator, home-made filter board with bias-tees)
- UHV chamber (viewports, electrical access, precision leak valve, beryllium ovens, ion gauge, and getter/ion pump)
- Objective lens (custom, Sill Optics)
- EMCCD camera (Andor iXon3 885)
- Photomultiplier tube (Hamamatsu H10682-210)
- Time-of-flight mass spectrometer (under construction, target completion March 2018)
  - Photonis LongLife Micro-Channel Plate
  - Home-made electrodes and electrostatic lenses

### Lasers and accessories

- 313 nm cooling laser for Be<sup>+</sup>
  - 36 mW max output, tunable
  - Beamline includes AOMs with DDS drivers for tuning and pulsing the laser
- Pulsed, doubled dye laser at 301 nm for O<sub>2</sub> photoionization
  - Quantel 660B Nd:YAG pump (120 mJ at 532 nm, 10 ns, 20 Hz)
  - Quantel TDL60 oscillator with two amplification stages ( $\sim 0.08 \text{ cm}^{-1}$  bandwidth)
  - Continuum UVX doubler with tuning tracker
  - Neslab System II heat exchanger for chilled water
- 235 nm for Be photoionization and O<sub>2</sub><sup>+</sup> photodissociation (under construction, target power 2 mW, target completion January 2018)
- Burleigh WA-1500 wavemeter (0.2 ppm accuracy)
- Burleigh WA-4500 pulsed wavemeter  $(0.02 \text{ cm}^{-1} \text{ accuracy})$
- Home-made wavemeter with 0.1 ppm resolution (shared)
- Two scanning Fabry-Perot cavities for transferring long-term stability (< 3 MHz/day) from a stabilized HeNe to a diode laser
- Stabilized HeNe laser (2x Melles Griot 05-STP-901, 1x HP 5517B)
- Infrared viewer (FJW Find-R-Scope)
- Power meter with sensors (Thorlabs PM100D, S121C, S120VC)
- Optical tables  $(4' \times 10', 4' \times 6', 3' \times 8')$

### Test and measurement equipment

- Four computers with LabView and various interfaces (ethernet, GPIB, RS232)
- DAQ boards (NI USB-6001, NI USB-6343)
- Various oscilloscopes (e.g. Agilent DSO-X 2004A)

- Benchtop and handheld digital multimeters
- Various linear DC power supplies (e.g. Instek GPS-4303)
- Spectrum analyzer (HP 8563A, shared)
- Vector network analyzer (Keysight E5063A, shared)

## Precise and accurate radiofrequency equipment

- GPS-disciplined rubidium oscillator (SRS PRS10 with SynPaQ/E-M12M-T receiver)
- 10 MHz distribution amplifier (Symmetricom 6502)
- Direct digital synthesizers
  - Enterpoint Milldown boards (4)
  - Four channels of AD9910 DDS's per board
  - Each channel with Analog Devices ADL5330 variable-gain amplifier
  - Each board with a Xilinx Spartan 6 controller
  - Capable of real-time frequency, phase, and amplitude control
  - We have a total of 16 channels
- Various commercial synthesizers (HP 8648B, HP 8656B, Rigol DG4062)
- Various rf power amplifiers and other components (mixers, splitters, filters, detectors)

## Other equipment

- Turbo pumping station: Agilent TwisTorr 84 FS turbo (67 L/s), IDP-3 scroll pump
- Pulsed supersonic beam apparatus (under construction, target completion March 2018)
  - Parker Series 9 valve
  - Beam Dynamics skimmer

Finally, we note that we do not anticipate any delay in the start of this project due to moving to the new science center in the summer of 2018. The current apparatus was designed with an anticipated future move. For example, as many optical systems as possible are modular and mounted on smaller optical breadboards that are attached to the larger optical table rather than having individual components bolted to the large table directly. The College has been proactive in mitigating any potential consequences of construction and moving.

## Data Management Plan

#### Data content and collection

Our data constitute the scientific record of our endeavors, and we take its management seriously. The data in our lab arise from two primary sources: the construction and modification of the apparatus and the science. The documentation of both is conceptually similar, though the actual process is more automated for the science data.

The apparatus-related data involve a person making a change that is documented in a log. We primarily keep our logs online in two forms: a blog and a wiki. The blog, based on the WordPress software, is our lab notebook. It typically contains daily entries or perhaps several per day that document precisely what we do and why. It is accessible via password from across campus and via VPN from around the world. It is searchable and allows uploading of images and documents. Every member of the group has their own personal blog and can read and comment on every other blog. The wiki, based on the MediaWiki software, is our repository for lab knowledge. Once a device works, this is where you put the instructions. Since working in this lab will be the first research experience for most students, we take care in instructing them in proper data collection techniques and the importance of writing *everything* down. (And not on scrap paper!) Because some tasks are necessarily done away from a computer, we still issue each student a paper notebook that supplements the online log.

The science data consist of at least one of the following (1) images of ion crystals, (2) digitized microchannel plate events, and (3) photon counts from the Be<sup>+</sup> ions, registered as pulses from a photomultiplier tube. Each event is logged in our data acquisition software and is accompanied by significant metadata, including a time-stamp. For example, if the data were acquired at the end of a particular laser pulse sequence, we automatically keep copies of the software that programmed the sequence and the hardware state during the experiment. Because the quantity of data is modest compared to hard-drive sizes, the storage of the computer-generated data is in simple ASCII files.

#### Data storage and preservation

Data, the blog, the wiki, and the LabView and Python programs reside locally on desktop computers in the lab. The computer hosting the blog and wiki has its hard drives mirrored using RAID. All other lab computers automatically back up to this server daily. The server, in turn, automatically backs up daily to a hard drive elsewhere on campus.

In an effort to instruct the students about data preservation, we have a laboratory policy that the wiki may be continually revised to show the state of our current knowledge, but the blog should not be changed as it is the record of events as they were *when written*. In the case of egregious error, one may alter a post by placing a strike through the offending text (the equivalent of an X in a paper notebook), but the original record must remain. Nonetheless, both the wiki and the blog keep versioning logs so all changes to inputs are recorded.

Aside from personnel documents, we do not expect any data that requires special handling because of its sensitive nature. Our Human Resources office is the primary caretaker of personnel files.

### Dissemination

Formal dissemination will be via publications and presentations. My students, postdoc, and I will present the results of this work in colloquia and at conferences, both by talk and poster. We will publish our results in widely accessible journals as well as on the arXiv preprint server. Amherst College maintains an open-access collection of all scholarly work produced by its faculty<sup>1</sup>. On my personal web site<sup>2</sup>, I post links for all my papers to the publisher's web site and the arXiv. Whenever allowed by publishers, I post the original journal article. Conference posters are accessible online as well. Senior theses are posted on my web site and the department's web site<sup>3</sup> and are archived in the College's library.

We also seek ways to informally disseminate our work. The atomic physics community is a generally friendly one. We have benefited from the sharing of both data and "tricks of the trade", and we happily give back as we develop tricks of our own.

We will provide data to other researchers upon request. In the past, we have provided others with both raw data and analyzed data that went into a figure.

<sup>&</sup>lt;sup>1</sup>https://acdc.amherst.edu/collection/octagon

<sup>&</sup>lt;sup>2</sup>https://dhanneke.people.amherst.edu/publications.shtml

<sup>&</sup>lt;sup>3</sup>https://www.amherst.edu/academiclife/departments/physics/alumni/senior\_theses

## Postdoctoral Researcher Mentoring Plan

The role of a postdoc at Amherst College is both similar to and different from that at a major research university. The primary purpose of the position is to participate in a world-class research program and to mature towards being an independent scientist. Since we are at a small college, however, I will encourage participation in the other aspects of college life, including the educational aspects of our program such as mentoring undergraduates and possibly teaching.

The postdoc hired under this program will join a vibrant scientific and educational community. In addition to the faculty and regular staff, the Physics & Astronomy Department currently hosts three postdocs, a graduate student (formally affiliated with the University of Massachusetts), and a post-baccalaureate researcher. During the academic term, we have a weekly colloquium with outside speakers. Postdocs regularly attend the colloquium and meet with the speaker. Locally, Amherst joins Smith, Mount Holyoke, and Hampshire Colleges as well as the University of Massachusetts to form the Five College Consortium. These five colleges provide a broader community with many seminars and resources. The University in particular provides a network of other young scientists. I expect the postdoc to present at one or more conferences a year to keep in touch with the scientific community at large.

My mentoring of the postdoc as scientist will involve skills needed for success both in the lab and out. As needed, I will provide hands-on training in laboratory techniques, though I anticipate a good postdoc will have a number of skills to teach me as well. Training on the responsible conduct of research will be provided through the College's formal training, by calling attention to issues as they arise, and by example. I will seek opportunities for the postdoc to develop skills in scientific communication, including writing research papers and grant proposals as well as presenting results in seminars and conferences. I will mentor the postdoc on future career plans, including explicitly discussing those plans, helping them set goals related to the plans, and providing opportunities to meet their goals.

The liberal arts college environment presents unique opportunities for mentoring of the postdoc as educator. They will necessarily work closely with the undergraduates in the lab, presenting the postdoc with the chance to advise and mentor the students and me with the opportunity to mentor the mentor. The continuity of a multi-year postdoc will also help bring the students up to speed more quickly as they cycle in and out of the lab.

If the postdoc has an interest in teaching, I will work to give them the opportunity. In the past, postdocs have put together small courses on their graduate work or other topics and taught them to students during our three-week January interterm. Other postdocs have been integrated more formally into our classes as instructors in teaching labs or discussion sections.



AMHERST COLLEGE Office of the Controller

# Certification of RUI/ROA Eligibility

By submission of this proposal, the institution hereby certifies that the originating and managing institution is an accredited college or university that awards Associate's degrees, Bachelor's degrees, and/or Master's degrees in NSF-supported fields, but has awarded 20 or fewer PhD/DSci degrees in all NSF-supported fields during the combined previous two academic years.

Authorized Organizational Representative: Stephen Nigro, Controller

Date: 10.10.2017 Signature:

### **RUI Impact Statement**

#### Research at Amherst College

Amherst College is a small, highly selective, liberal arts college located in western Massachusetts. We have approximately 1,850 students and 200 faculty members. Our college has a strong commitment to research and to engaging students in active questions at the forefront of knowledge. The sciences at Amherst attract significant external funding, including 15 active NSF awards and a total of \$9.4 million over the past five years to support research in STEM and the social sciences. The challenging work set out in this proposal is well-matched to Amherst.

The Physics & Astronomy Department has eight tenure-line faculty members. We are engaged in work on precision measurements with trapped molecular ions (David Hanneke), topological features in Bose-Einstein condensates (David Hall), local Lorentz invariance and laser-cooling molecules (Larry Hunter), quantum nanomagnets (Jonathan Friedman), DNA folding (Ashley Carter), direct-imaging of exoplanets (Kate Follette), neutrino scattering theory (William Loinaz), and field theory and the foundations of physics (Kannan Jagannathan). Each of the faculty members doing experimental work has external funding. Ashley Carter and I have current NSF CAREER grants.

The quality of the work in the Physics & Astronomy Department has been recognized with national awards. David Hall and Larry Hunter have received the APS Prize for a Faculty Member for Research in an Undergraduate Institution (in 2012 and 1991). Student Benjamin Heidenreich was a finalist for the APS Apker Award for undergraduate research in 2006. Former undergraduates Michael Foss-Feig and Adam Kaufman have gone on to win the 2013 and 2016 awards for Outstanding Doctoral Thesis Research in AMO Physics (now the Jin Prize). My current thesis student Alexander Frenett received a Goldwater Scholarship in 2017.

### Student involvement in research

Research involvement is an important part of many students' education at Amherst. It emphasizes that science occurs primarily outside the classroom. It develops skills that complement those learned through coursework. It gives a taste of research for those considering grad school.

Students can get involved as early as their first year. Most initially notice the research culture through the posters that line the hallway, the weekly colloquium, or the examples used in the classroom that are drawn from work done on campus. The college holds a competition for Summer Undergraduate Research Fellowships (SURF) that are only available for students completing their first or second year. These fellowships come with ten weeks of funding and include many social events and seminars on topics like programming languages, how to make a poster, or research ethics. There is a poster session in the early fall to celebrate the students' work.

About 75% of our physics majors write a senior honors thesis. An honors thesis at Amherst is a substantial undertaking, comparable to a masters-level work at some institutions. The time investment is equivalent to three of eight courses in the senior year. Most students spend part of the prior summer getting started, and the college typically provides support for eight weeks of summer work. I often use NSF funding to bring this up to ten weeks of support. My own work has involved 27 students over 6.5 years. Seven of them have completed senior honors theses, and two theses are currently underway. Table 3 lists my thesis students and what they did after graduation. Six of my thesis students have been co-authors on publications, which I indicate with an asterisk on my biographical sketch. I expect the work of my current two thesis students will lead to publications as well.

Student	Thesis title	After graduation		
Alex Frenett '18	Still in progress, time-of-flight mass spectrometry and supersonic beams	applying to physics grad school		
Christian Pluchar '18	Still in progress, construction of a 235- nm laser for beryllium photoionization and $O_2^+$ photodissociation	applying to physics grad school		
David Lane '17	Developing a Quantum Toolbox: Experi- ments with a Single-Atom Harmonic Oscil- lator and Prospects for Probing Molecular Ions	Gap year then grad school		
Ned Kleiner '16	Quantum Control of Be <sup>+</sup> Ions	Harvard Earth and Planetary Science Ph.D. program		
Jiajun Shi '15E	Radiofrequency Synthesis System for Laser Modulation	Caltech electrical engineering M.S.		
Phyo Aung Kyaw '14	Constructing an Ultra-High Vacuum Cham- ber and a Radio Frequency Helical Resona- tor for Trapping Ions	Dartmouth electrical engineer- ing Ph.D. program		
Chu Cheyenne Teng	Frequency Control and Stabilization of a	Princeton electrical engineering		
'14E	Laser System	Ph.D. program		
Shenglan Qiao '13	Constructing a Linear Paul Trap System for Measuring the Time-variation of the Electron–Proton Mass Ratio	Stanford physics Ph.D. program		
Celia Ou '13	Third Harmonic Conversion	UC San Diego, Scripps Institu- tion of Oceanography Ph.D. pro- gram		

Table 3: Undergraduate honors theses supervised. An "E" on the class year indicates a December graduation ('14E is Dec. 2013).

## Commitment to diversity

Amherst College is committed to maintaining a diverse student body. Over many years, the college has worked to increase student diversity. This work has paid off. Of American students at Amherst, 45% self-identify as students of color and 34% self-identify as minorities that are underrepresented in the nationwide population of college students. We are a national leader on economic diversity and have a need-blind admission policy and a commitment to meet the need of any admitted student without the use of loans. We are one of very few schools that extends this commitment to international students.

Amherst is also committed to increasing the diversity in STEM fields. At a White House Summit on STEM access in January 2014, our college president committed us to "Increase the proportion of low-income and disadvantaged Amherst students who major in science and math fields." We maintain an extensive support network for these students as we work towards that goal. We run a "Summer Science" program that brings first-generation and/or low-income students to campus for several weeks before their freshman year. They do some work on building quantitative skills, but the main purpose is cohort-building and an introduction to life at the college. Support continues through the year with a Quantitative Skills Center staffed with a faculty director, fulltime staff associate director, and several full-time associates and fellows. Select students are invited to participate in an "intensive advising" program in which they meet with a faculty advisor twice a month instead of once a semester. I am participating as an advisor in this program and have found it fruitful in helping my advisees work through their unique challenges at getting acclimated to college life. The Amherst Association of Women in Science is one of the larger student groups on campus and is active in training student mentors, hosting discussions with faculty, and holding alumni panels to discuss careers in STEM.

## Particular impact of this project

This project will have a particularly strong impact on the training of three to five students who will do their honors thesis on this topic, an additional 6–15 students who will work on it over the summer or during the academic term, and a postdoc who will use it as a stepping stone on a scientific career. It will also impact my own career by allowing me to build on the foundation laid by my CAREER grant.

Through this work, students will be introduced to topics such as

- Lasers and electro-optical techniques
- Optical frequency metrology
- Molecular clocks
- Atomic and molecular physics, including evaluation of systematic effects
- Computer programming, simulation, and data analysis
- Computer-assisted design, such as SolidWorks

I am particularly excited to bring optical frequency metrology to our college. This is a vibrant and growing field, and I look forward adding a few orders of magnitude of precision to our work.