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YIP – Ultrasensitive Infrared Spectroscopy of Molecular Ions of Importance in Atmospheric
Chemistry and Propulsion

(Award Number FA9550-07-1-0128)

Principal Investigator:

Prof. Benjamin J. McCall
Departments of Chemistry, Astronomy, and Physics
University of Illinois at Urbana-Champaign
600 S. Mathews Ave.
Urbana, IL 61801

Program Manager:

Dr. Michael R. Berman
AFOSR/NA
875 N. Randolph Street
Suite 325, Rm 3112
Arlington, VA 22203

(submitted electronically)

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14. ABSTRACT The objective of this effort has been to develop a novel instrument for the spectroscopic study of molecular ions, which we call SCRIBES (Sensitive, Cooled, Resolved, Ion BEam Spectroscopy). The instrument has been constructed during the period of this award, and ultrasensitive spectroscopic techniques (including NICE-OHMS) have been employed in an effort to obtain an absorption spectrum of the N2+ molecular ion. While the SCRIBES instrument is still being commissioned, this work has already led to the development of an unexpected and exciting approach for molecular ion spectroscopy: cavity-enhanced velocity modulation spectroscopy.					
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Objectives: The primary objective of this research effort has been to develop a novel instrument for the spectroscopic study of molecular ions, which we call SCRIBES (Sensitive, Cooled, Resolved Ion BEam Spectroscopy).

Status of Effort: Our first generation ion beam instrument, completed in 2008, lacked the diagnostics necessary to optimize the overlap between the ion beam and the laser beam in our cavity. On the advice of Dr. Holger Kreckel, who is now a research scientist in our group, we completely redesigned the system to be modular in nature, and to accommodate adjustable apertures and ion beam profile monitors. We also switched from quadrupoles to cylindrical benders to improve the collimation of our ion beam. Furthermore, we built and integrated a beam-modulated time-of-flight spectrometer to aid in beam diagnostics. This second-generation instrument was completed in May of 2009, and was a marked improvement over the first generation.

However, we quickly found that the noise level in our laser spectrometer was too high to observe the weak ion signals in the ion beam. We had been using a highly-sensitive technique called continuous-wave cavity ringdown spectroscopy, and even implemented a novel modulation scheme which allowed us to reach down to a minimum detectable absorbance in the 10^{-10} cm^{-1} range. But we were unable to detect any spectral lines of N_2^+ (our test molecule), and we could not further improve the sensitivity because of vibrations caused by the pumps in our system.

In July 2009, we undertook two major initiatives to resolve these problems. First, we decided to rebuild the ion beam instrument on a separate platform, in order to decouple it from the laser table where the laser system and cavity rest. This work was completed in late 2009, and as a result the instrument worked better than ever before. We also took that opportunity to lengthen our time-of-flight region, and perform some electronic upgrades to offer us higher mass and energy resolution in our mass-spec. This has provided us with real-time diagnostics of the ion beam's absolute energy and energy spread, which will aid in our spectroscopic efforts. Indeed, we found that because of an unexpectedly large plasma shift in our ion source, we were probably scanning at the wrong frequency before!

Our second major initiative of 2009 was to abandon cavity ringdown spectroscopy and implement an even more sensitive spectroscopic approach which required locking our cw laser to a moderate-finesse optical cavity, which we would ultimately place around our ion beam. We began this effort by using our laser's internal piezos to lock the laser frequency to our cavity. To test the effectiveness of this approach on the spectroscopy of N_2^+ , we placed an AC positive column discharge cell inside the cavity and scanned for lines of N_2^+ . Much to our surprise, we were able to perform velocity modulation spectroscopy even inside an optical cavity, which was previously thought not to be possible. A paper discussing this serendipitous discovery was published earlier this year in *Optics Letters*. This approach offers the promise of greatly improving the sensitivity of traditional molecular ion spectroscopy of positive column plasmas.

In early 2010 we managed to improve our locking scheme substantially by using a piezo on our external cavity to stabilize the cavity length to be in resonance with the laser, and adding an acousto-optic modulator (driven by a voltage-controlled oscillator) to make fast frequency corrections to the laser to account for vibrations that are faster than the cavity piezo can servo out. This scheme has reduced our effective spectroscopic linewidth from over 100 MHz down to perhaps 10 MHz or so. A follow-up paper that combines this "cavity-enhanced velocity modulation spectroscopy" technique with ultra-precise frequency calibration using an optical frequency comb is now in final preparation for submission to *Chemical Physics Letters*.

Most recently, we have even further improved the sensitivity of our spectroscopy, by incorporating heterodyne modulation with our moderate-finesse cavity, in an approach called NICE-OHMS (Noise-Immune, Cavity-Enhanced Optical-Heterodyne Modulation Spectroscopy) that was developed by Jun Ye and Jan Hall at JILA. This method should allow us to approach the shot-noise

limit at high (~ 1 GHz) modulation frequencies, and still enjoy the signal enhancement of the cavity. Right now we are not yet at the shot-noise limit, but we are already a factor of ~ 10 more sensitive than with our non-heterodyne techniques!

However, even with NICE-OHMS, we were unable to see a signal from N_2^+ in our ion beam! Since we were at our wits' end as to how to improve the spectroscopy, we figured there must be some problem with the ion beam itself. We decided to make a beam of H_3^+ and attempt a photodissociation experiment, to better characterize the beam. Much to our surprise, our mass spectrometer showed only H_2^+ (hardly any H_3^+ at all) being extracted from our source when running a hydrogen discharge!! This implies that the extracted ions suffer no collisions inside the source (if they did, the H_2^+ would immediately react with H_2 to form H_3^+). Presumably the same was happening in a nitrogen discharge – although we were making lots of N_2^+ ions, they never suffered collisions to be thermalized, so they were certainly very excited rotationally, vibrationally, and even electronically. Very few ions would have been in the ground states that we were probing spectroscopically, which explains our lack of an absorption signal.

We have since discovered that by reversing the polarity of the discharge, we are able to extract ions that have suffered many collisions. In a hydrogen discharge, we can now produce almost exclusively H_3^+ , which suggests that we would also produce thermalized N_2^+ in a nitrogen discharge. We are just now in the process of searching for a signal from N_2^+ with NICE-OHMS, and we are very optimistic that we will at last succeed!

Once we observe N_2^+ , we plan to switch back to using our difference frequency laser (which we have already used for extensive spectroscopy of H_3^+ in a separate program), and begin performing spectroscopy on the real ions of interest in the mid-infrared.

Accomplishments/New Findings: Most of our accomplishments to date are technical in nature. To summarize, we now have a mature mid-infrared laser system, we have performed very high sensitivity spectroscopy and are continuing to improve on that aspect, and we have made many improvements to our ion beam system. Separately, we have built a very stable supersonic expansion ion source that we are now spectroscopically characterizing using H_3^+ , and early indications are that the ions are cooling effectively. We expect that major spectroscopic results will be forthcoming in late 2010 and early 2011. Ultimately, we expect that our ion beam system, coupled with the difference frequency laser, will be able to study a host of molecular ions of interest to the Air Force. Our major scientific finding to date is the discovery of “cavity-enhanced velocity modulation spectroscopy,” and is the subject of a recent paper in *Optics Letters* and a manuscript including frequency comb calibration that will soon be submitted to *Chemical Physics Letters*.

Personnel Supported: During the past roughly three years, this award has supported the salary of graduate student Brian Siller, who has led the effort to lock our cw lasers to external cavities, in order to enable very high-sensitivity spectroscopy. It has also supported a fraction of the PI's summer salary. Since November 2008, it has also supported a new postdoctoral fellow (Manori Perera, from Rick Metz's lab) who has played a major part in the characterization of the new ion beam system, and spearheaded the successful design and implementation of our mass spec. Graduate students Andrew Mills, Kyle Ford, and Kyle Crabtree have also been actively involved in the work described in this report, although they have been supported by other funds. We have also successfully recruited a senior researcher (Holger Kreckel, Ph.D. from MPI Heidelberg) who is an expert in ion optics and laser spectroscopy; although he has been supported by other funds (my Packard Fellowship), he is taking on the leading role on the ion beam experiment.

Publications: Air Force Lt. Col. Brian Tom, a graduate student in our group, had a Communication published in the *Journal of Chemical Physics* ([130](#), 031101, 2009); this paper represents the first result

from the difference frequency laser system that will be used with our ion beam machine. He has also had a Note published in *Review of Scientific Instruments* (**80**, 016108, 2009), which describes our para-H₂ generation and characterization methods. In terms of publications that are directly tied to the work supported by this award, we have published a paper in *Optics Letters* (**35**, 1266, 2010) and are about to submit a follow-up paper, on cavity-enhanced velocity modulation very soon. We also envision a detailed instrument paper on our ion beam spectrometer within a few months, once an N₂⁺ spectrum is in hand.

Interactions/Transitions: Over the course of this award, this research effort has been the centerpiece of two posters and a talk at the Air Force Molecular Dynamics Contractor's meeting, and was a major component of the PI's Coblentz Award Lecture at the 64th International Symposium on Molecular Spectroscopy. It has also been discussed in seminars at Columbia University, Texas A&M University, Indiana State University, the University of Wisconsin at Madison, the Massachusetts Institute of Technology, the Harvard-Smithsonian Center for Astrophysics, the University of Southern California, the California Institute of Technology, and Stanford University. It will also be featured prominently in a seminar next month at the University of Colorado at Boulder.

New Discoveries, Inventions, or Patent Disclosures: None.

Honors/Awards: During the grant period, I have received a Sloan Research Fellowship, a Cottrell Scholar Award from the Research Corporation, and a Dreyfus Teacher-Scholar Award, in part to support our work on the ion beam system. I have also been appointed a Beckman Fellow of the UIUC Center for Advanced Study. I was also awarded the 2009 Coblentz Award at the 64th International Symposium on Molecular Spectroscopy. Prior to this effort, I was selected for a Presidential Early Career Award for Scientists and Engineers (PECASE) by the White House.