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ABSTRACT

Molecular ions play a pivotal role in the chemistry of the interstellar medium due to their high reactivity even at low temperature. To identify these ions in interstellar space, it is essential to obtain high resolution laboratory spectra of potential interstellar ions for comparison to observational data. At the University of Illinois, we are developing a Sensitive, Cooled, Resolved Ion BEam Spectrometer (SCRIBES) that will allow us to obtain high resolution infrared direct absorption spectra of rotationally cold molecular ions in the absence of neutral molecules. This instrument can overcome many of the problems that arise when using other spectroscopic techniques. It benefits from the high sensitivity of cavity enhanced techniques and accurate laser frequency calibration using a frequency comb. Currently, we are using a cold cathode ion source to produce an N_2^+ test beam that will be studied using SCRIBES.

1. Introduction

More than 150 molecules have been observed in the interstellar medium (ISM) to date. The vast majority of these molecules are formed by ion-neutral reactions at low temperatures and low densities. New telescopes such as Herschel and SOFIA will obtain spectra at previously unavailable frequencies in the sub-mm/far-infrared range with high-resolving power

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to study the molecular composition of the universe. This will necessitate extensive laboratory work to identify new molecules or classes of molecules responsible for astronomically observed transitions in these frequency domains.

Compared to neutral molecules, relatively few high resolution spectra of molecular ions have been obtained in the laboratory. This is due to experimental difficulties as, e.g., low number densities, high temperatures in laboratory plasmas, and spectral confusion due to neutral species. In addition to these obstacles in creating and isolating the ions, studying them at THz frequencies is also not a simple task. Although the availability of THz light sources is improving, the experimental difficulties related to their operation are still significant. Alternatively, we can use mid-IR spectroscopy – benefitting from the availability of mid-IR light sources and the accuracy of frequency combs – to indirectly acquire THz spectra by studying combination differences to infer rotational level spacings. In this article, we will discuss the research conducted at the University of Illinois, where we are developing a Sensitive, Cooled, Resolved Ion BEam Spectrometer (SCRIBES) and various high resolution spectroscopic techniques to acquire indirect THz signatures of molecular ions.

2. Instrumentation and Spectroscopy Techniques

An overview of the SCRIBES instrument is shown in Fig. 1. A fast molecular ion beam (4 kV) will be extracted from a supersonic ion source (described in detail by Crabtree et al. (2010)) and guided into the overlap region by dedicated ion optics. In the overlap region the ions will be superimposed with a laser cavity for sensitive absorption techniques. A difference frequency generation laser will be used to produce IR radiation between 2.2 μm and 4.8 μm. For absolute frequency calibration a frequency comb will be coupled to the laser setup, to provide an accuracy that is orders of magnitude better than traditional wavemeter calibration. After the overlap region the ions enter a time-of-flight mass spectrometer (TOF-MS) that will allow for *in situ* characterization of the ion beam. In its final form, the instrument will offer the following advantages over previous techniques: (1) physical separation of ions and neutrals, (2) narrow linewidths due to kinematic compression in a fast ion beam, (3) reduced spectral congestion and low rotational temperatures using a supersonic ion source, and (4) high sensitivity due to modern cavity-enhanced spectroscopy methods.

We are exploring several spectroscopic techniques that can ultimately couple with SCRIBES to produce high resolution absorption spectra such as cavity ringdown spectroscopy (CRDS), cavity enhanced velocity modulation spectroscopy (CEVMS), and noise immune cavity enhanced optical heterodyne molecular spectroscopy (NICE-OHMS). Previous work in our lab has shown the sensitivity of CRDS (by Weaver et al. (2008)) and

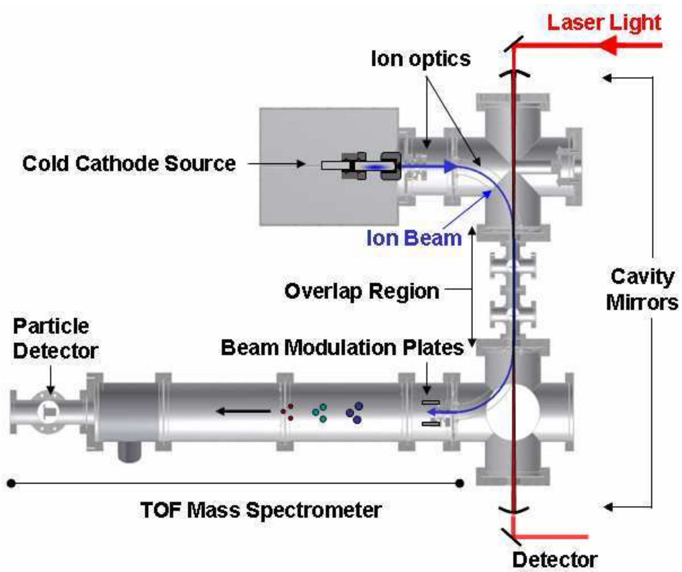

Fig. 1.— A schematic of SCRIBES with a cold cathode ion source.

CEVMS (by Siller et al. (2010) and Mills et al. (2010)) using a N_2^+ plasma in a positive column. Currently, we are studying N_2^+ plasma in a positive column using NICE-OHMS method to understand the signal shape and the sensitivity of the technique. Applying these techniques to a fast ion beam will provide a sufficiently high sensitivity and resolution to enable the use of combination differences to calculate THz transition frequencies (needed for astronomical observations) from our mid-infrared frequencies.

We have also characterized the ion beam properties using the TOF-MS. We found that the beam energy is different from the voltage source reading but has a low energy spread. Also, we found that the ions extracted from the cathode undergo fewer collisions than ions extracted from the anode. We determined this by studying a H_2 plasma and monitoring ions that are produced (see Fig. 2). The H_2^+ signal was reduced under conditions that favored collisions before extraction, because H_2^+ quickly reacts with H_2 to produce H_3^+. Based on these results, it seems critical to extract ions from the anode, in order to ensure that ions extracted from the source are thermalized.

3. Future Outlook

We are currently at the stage of combining SCRIBES with the NICE-OHMS setup to study a beam of N_2^+ ions. After finding the sensitivity and accuracy of our instrument

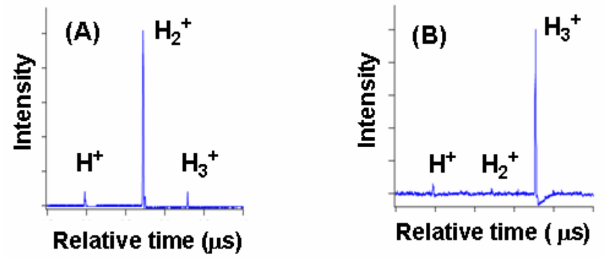

Fig. 2.— Mass spectra taken with a H_2 plasma show ions produced by a plasma with (A) less collisions when extracted from the cathode and (B) more collisions when extracted from the anode.

with the N_2^+ ion beam, we will use the ion HN_2^+, which has been extensively studied in the THz, to validate our procedures for interpreting our ultra precise IR spectra. We will then study known interstellar ions, such as HCS^+, HOC^+, HCO^+, CO^+, and $HCNH^+$ in the mid-IR frequencies. These frequencies then can be used with known microwave frequencies to acquire indirect THz frequencies.

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REFERENCES

Crabtree, K. N., Kauffman, C. A., & McCall, B. J. 2010, Rev. Sci. Instrum., 81, 086103

Mills, A. A., Siller, B. M., & McCall, B. J. 2010, Chem. Phys. Lett., 501, 1

Siller, B. M., Mills, A. A., & McCall, B. J. 2010, Opt. Lett., 35, 1266

Widicus Weaver, S. L., Wiczer, M. B., Negru, B., DiGangi, J. P.,Tom, B. A., & McCall, B. J. 2008, J. Mol. Spec., 249, 14
