High Resolution Spectroscopy of Molecular Ions: Development of an Instrument

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We are developing a versatile new technique called SCRIBES for high-resolution spectroscopy of molecular ions at low temperatures. The resulting spectra will enable direct searches for these ions in atmospheric, astrophysical, and combustion plasmas, and will serve as benchmarks for high-level theoretical calculations.

Motivations

Why Molecular Ions?

- **Astrochemistry:** Molecular ions drive an active chemistry at the very low temperatures and pressures of the interstellar medium.
- **Combustion:** Molecular ions are potential precursors to soot nucleation, and possible initiators of ignition outside of the usual combustion conditions.

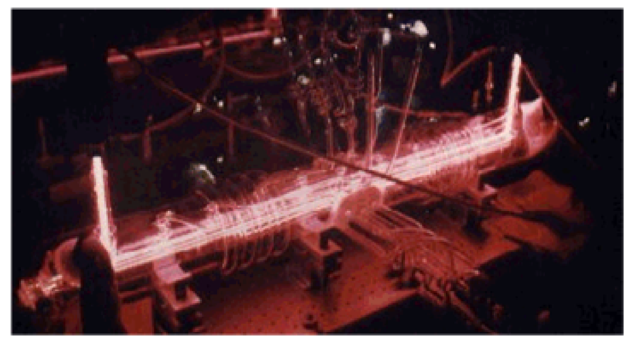
Why High-Resolution Spectroscopy?

- **Enabling Searches:** High resolution spectroscopy enables searches for molecular ions in the interstellar medium.
- **Benchmarks for Theory:** Spectroscopy is the gold standard for validating quantum chemical calculations.

How Can One Study Molecular Ions?

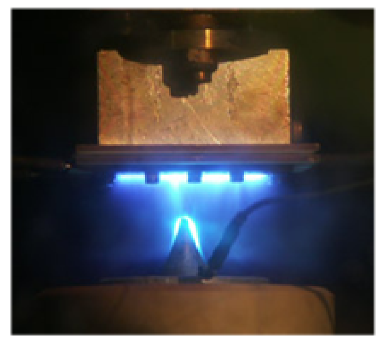
Two techniques have been widely used for molecular ion spectroscopy, but both have inherent limitations.

Velocity Modulation



Takeshi Oka (U. Chicago)

Supersonic Expansion



John Maier (U. Basel)

	Velocity Modulation	Supersonic Expansion	SCRIBES
High ion column density	✓		
Ion-neutral discrimination	✓		✓
Low rotational temperature		✓	✓
Sub-Doppler linewidth		✓	✓
Compatible with cavity-enhanced spectroscopy		✓	✓
Ultra-narrow linewidth from kinematic compression			✓
Mass spectrometry of spectroscopically probed ions			✓
Mass identification of spectral lines			✓

SCRIBES (Sensitive Cooled Resolved Ion BEam Spectroscopy)

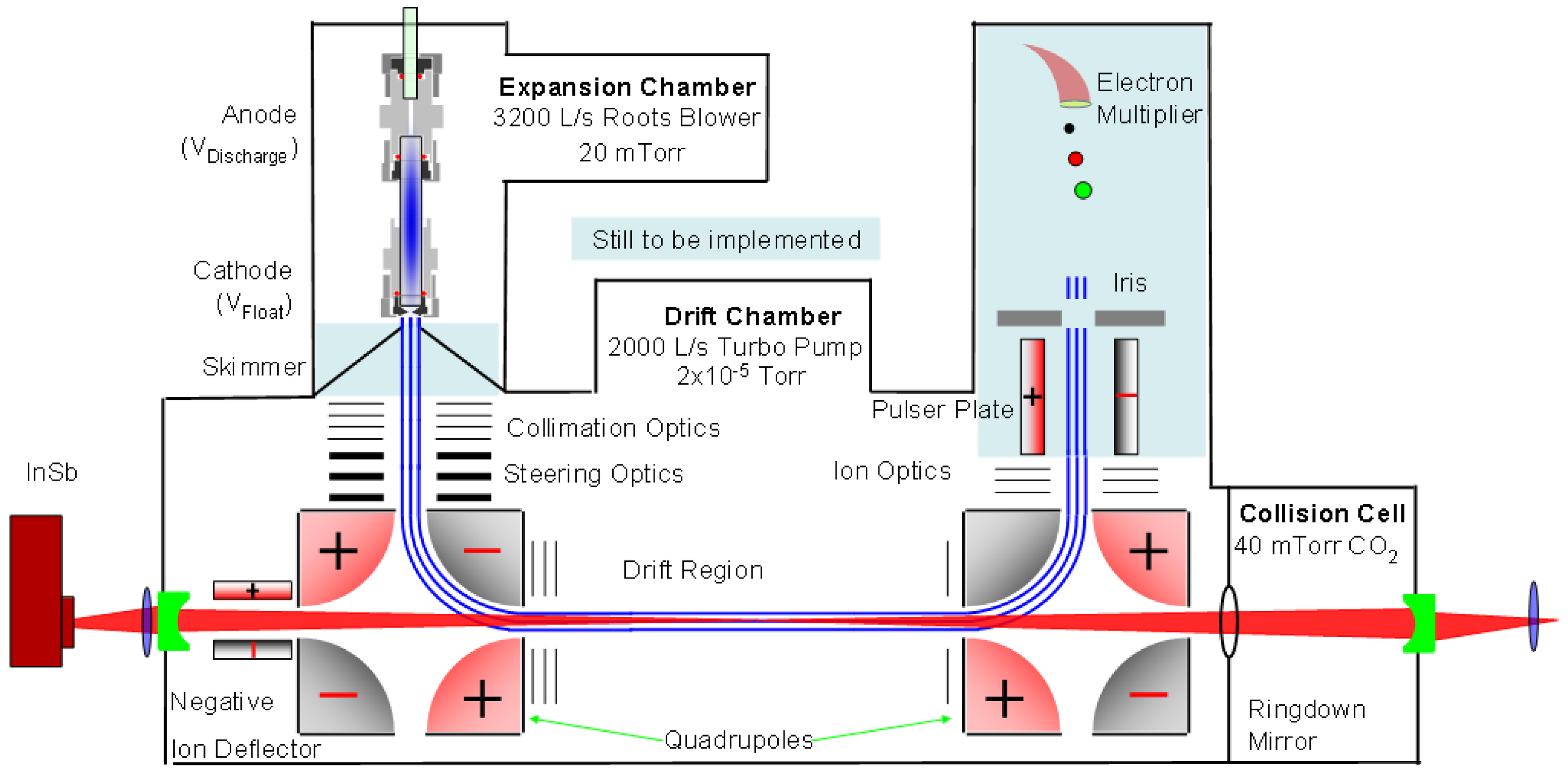
- Combining cavity ringdown spectroscopy, supersonic expansion, and fast ion beam technology
- Will enable spectroscopic study of complex, isolated molecular ions at low temperatures for the first time
  - **Sensitive:** Ultra-high sensitivity using cavity ringdown spectroscopy
  - **Cooled:** Continuous supersonic expansion discharge produces rotationally cold ions, greatly simplifying their spectra
  - **Resolved:** Ultra-high resolution from sub-Doppler line-widths due to acceleration cooling
  - **Ion BEam:** High voltage ion optics extract ions from neutrals into a fast ion beam, which can be probed using laser and mass spectrometry

Difference Frequency Laser

- We need a robust, widely tunable cw laser capable of scanning from ~3-5 μm, where most molecular ions have strong infrared transitions
- Combine tunable Ti:Sapphire laser and fixed Nd:YAG laser in periodically poled lithium niobate (PPLN) crystal
- Difference frequency $\nu_{IR} = \nu_{Ti:Sapph} - \nu_{Nd:YAG}$
- Measured 780 μW of narrowband cw-IR power tunable between 2.8-4.8 μm

Plan for Finishing Construction

- Use a nitrogen discharge.
- Use a diode laser to characterize the 2P-2S+ of N2+ in the ion beam
- Measure the line width, beam current, and make optimization procedures for the overlap of the two beams.
- Add time of flight mass spectrometer.
- Add supersonic expansion and differential pumping.
- Use DFG with ion beam.
- Lock DFG pump lasers to frequency comb to allow ultra precise and accurate frequency measurements of transitions.



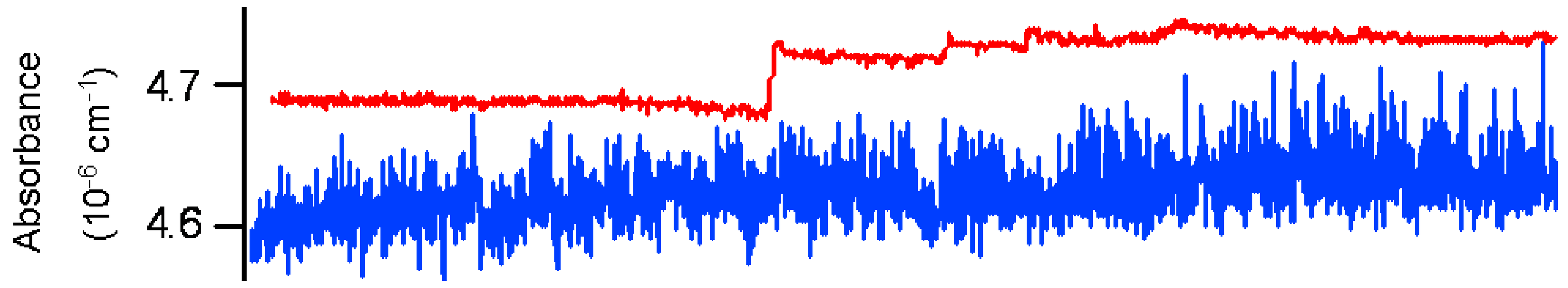
Recent Results

Collision with Background Gas

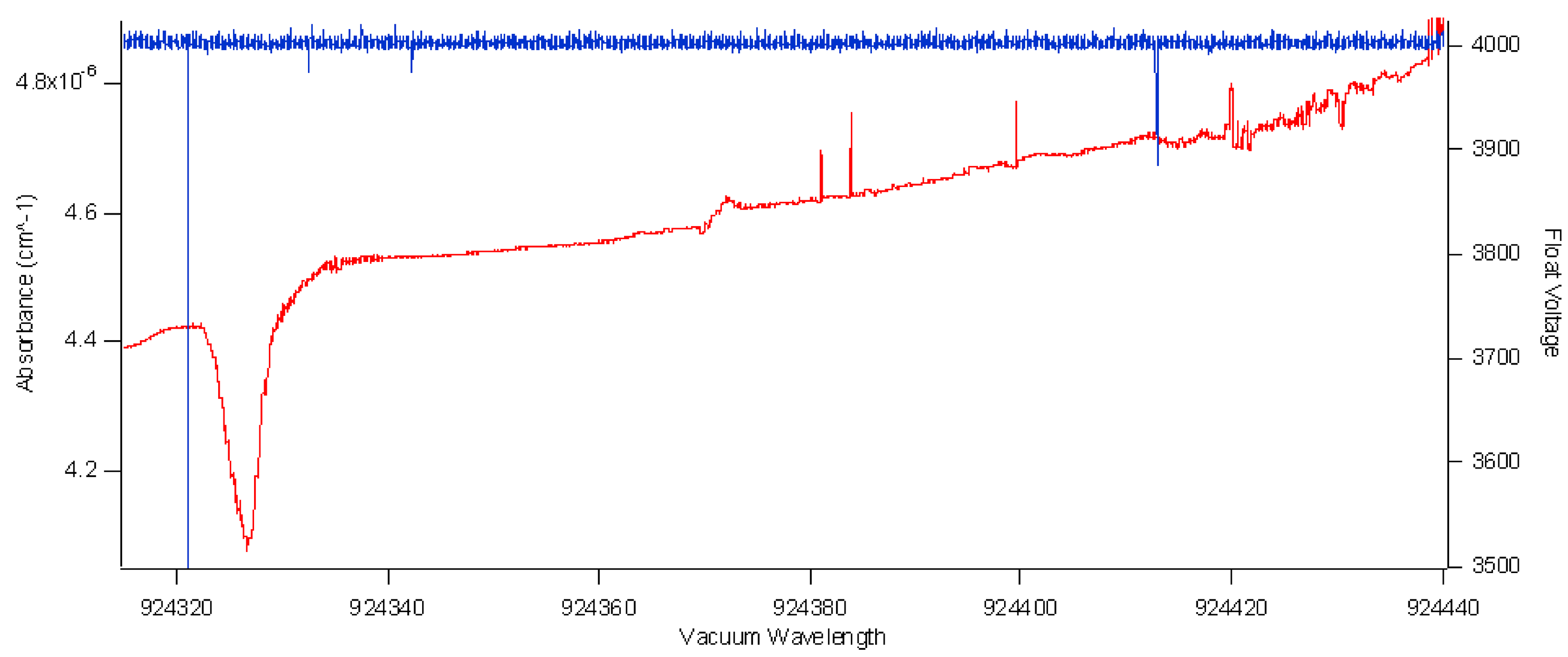
- We have discovered that the ions undergo a charge exchange interaction that to produce fast moving neutrals which damage the ringdown mirrors.

$$N_2^+ + N_2 \rightarrow N_2 + N_2^+$$

- A high pressure (50 mTorr) collision cell can reduce the damage to the ringdown mirrors
- The RED trace shows the absorbance increasing sharply as fast neutrals strike the ringdown mirror. At higher pressures, the damage becomes less. The BLUE trace shows 5 minutes and the absorbance does not change.



Preliminary Scan



Unknown Emission Peak, centered ad 924.326 nm. 1 GHz linewidth.

Future Work

- **Repeat measurement** Determine source of emission peak.
- **Finish stabilizing diode laser.** Current couple the diode laser for better scanning ability.
- **Finish N_2^+ characterization.** Determine linewidth.
- **Differential Pumping:**. To reduce the residual gas number and collisions.
- **Complex Molecular Ions:** Using SCRIBES, we plan to study larger and more complex ions than can be studied with velocity modulation. Examples include CH_5^+, $C_2H_3^+$, $C_2H_5^+$, $C_3H_3^+$, and $C_6H_7^+$.