New Approaches to Molecular Ion Spectroscopy

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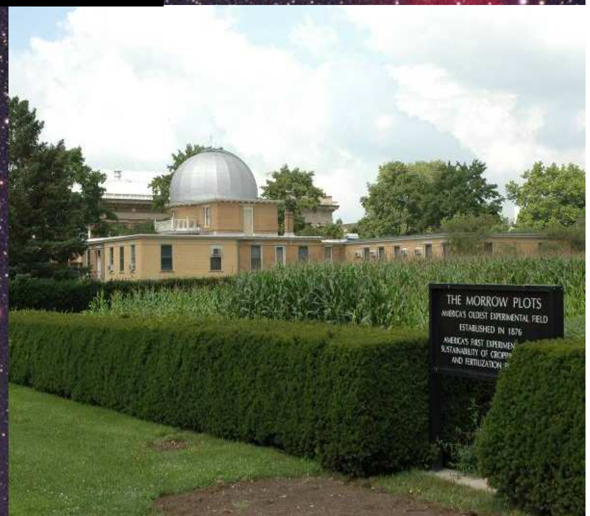

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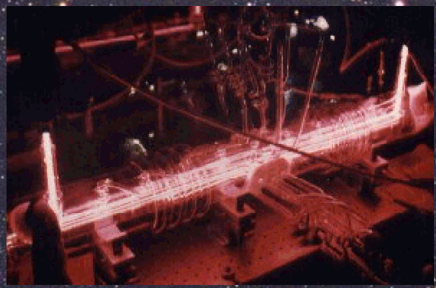
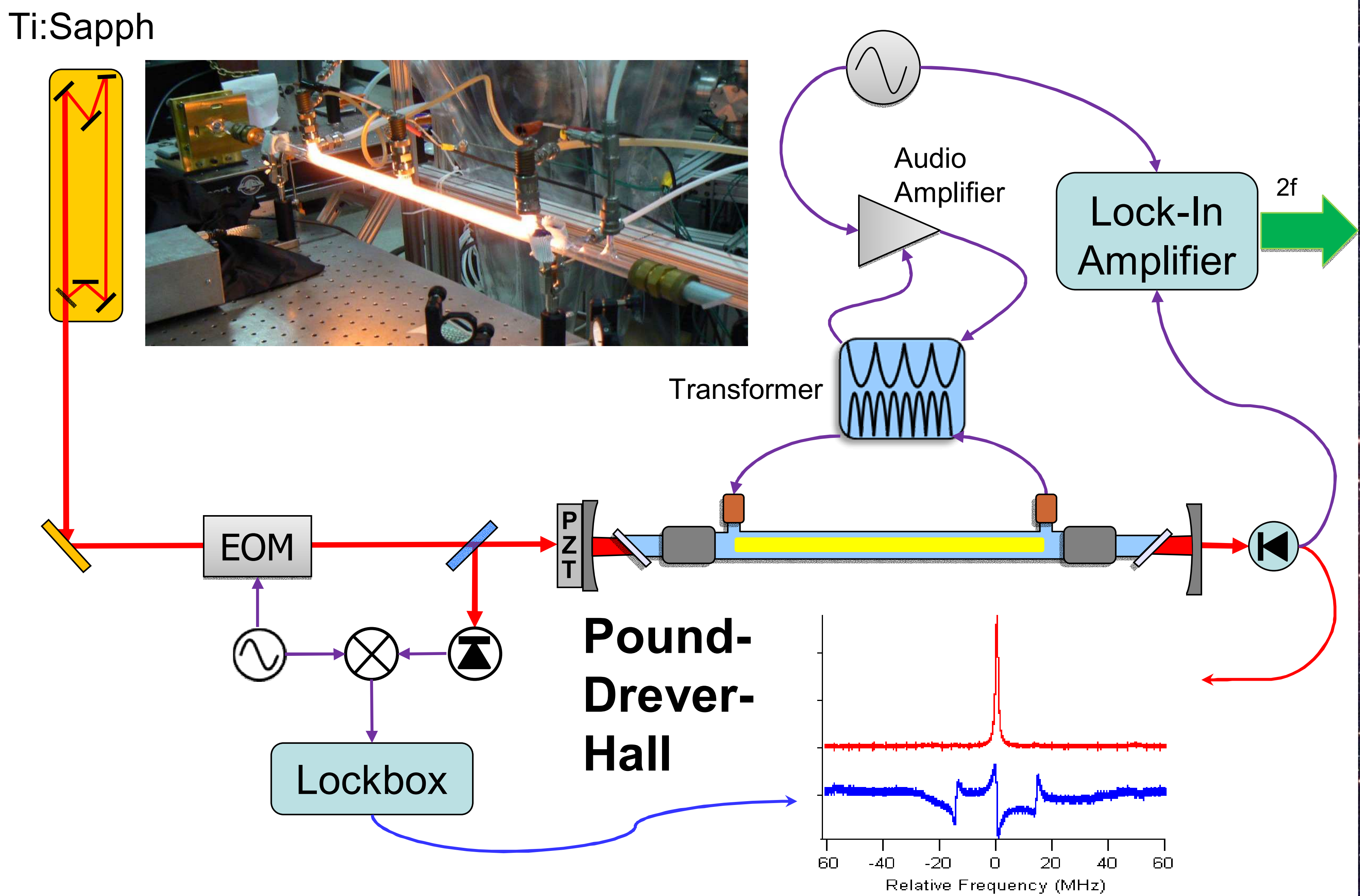
Ion Spectroscopy Techniques



	Velocity Modulation	Hollow Cathode	Supersonic Expansion
	Oka, Saykally	Hirota, Amano	Maier, Nesbitt
High ion column density	✓	✓	✗
Ion-neutral discrimination	✓	✗	✗
Low rotational temperature	✗	✓	✓✓
Narrow linewidth	✗?	✓	✓✓
Compatible with cavity-enhanced spectroscopy	✗?	✓	✓

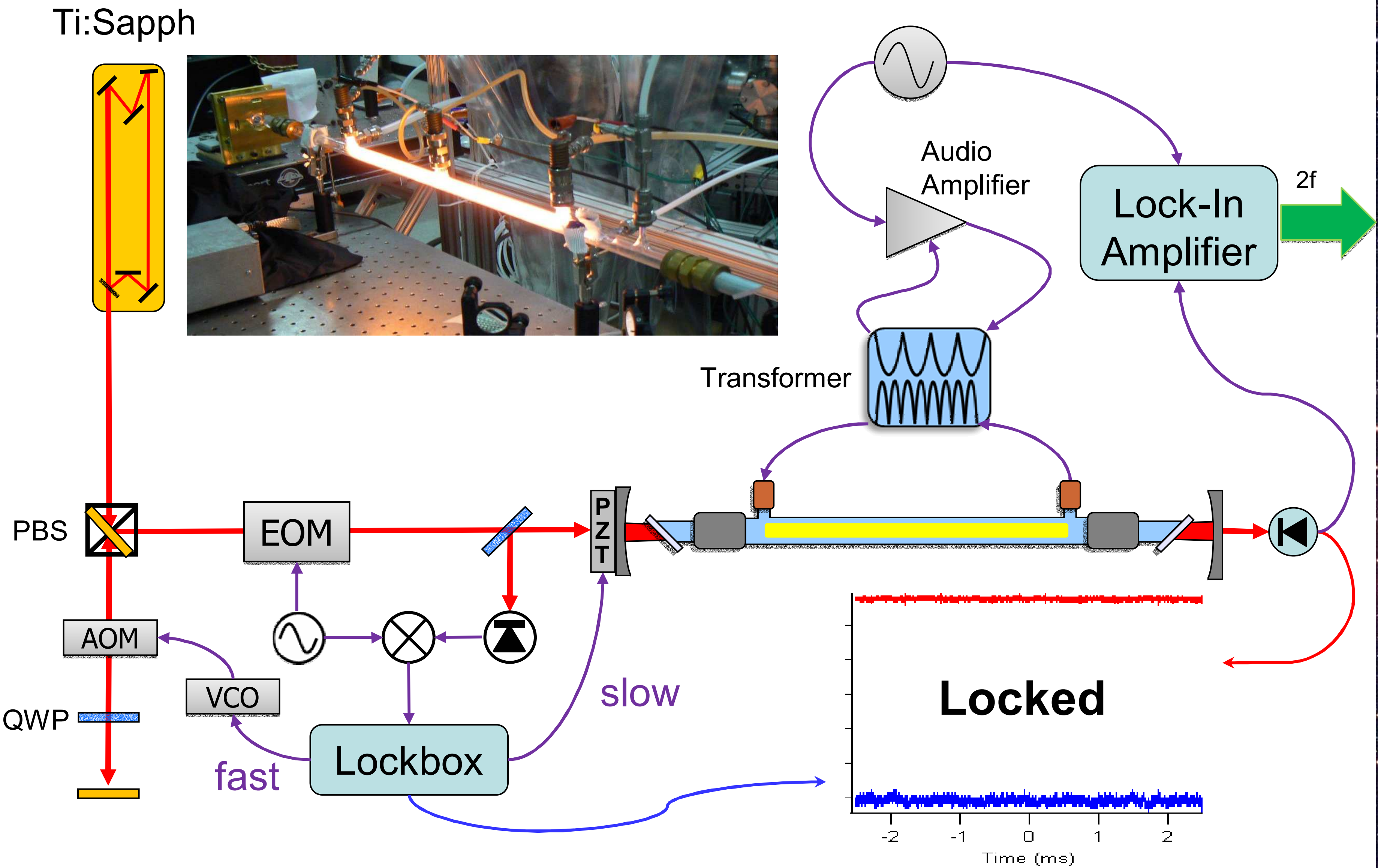
Each of the three main techniques for ion spectroscopy has advantages and disadvantages.
Velocity modulation is unique in offering discrimination between ion and neutral signals.
What if we could obtain narrow linewidths and cavity enhancement with velocity modulation?

Cavity-Enhanced Velocity Modulation



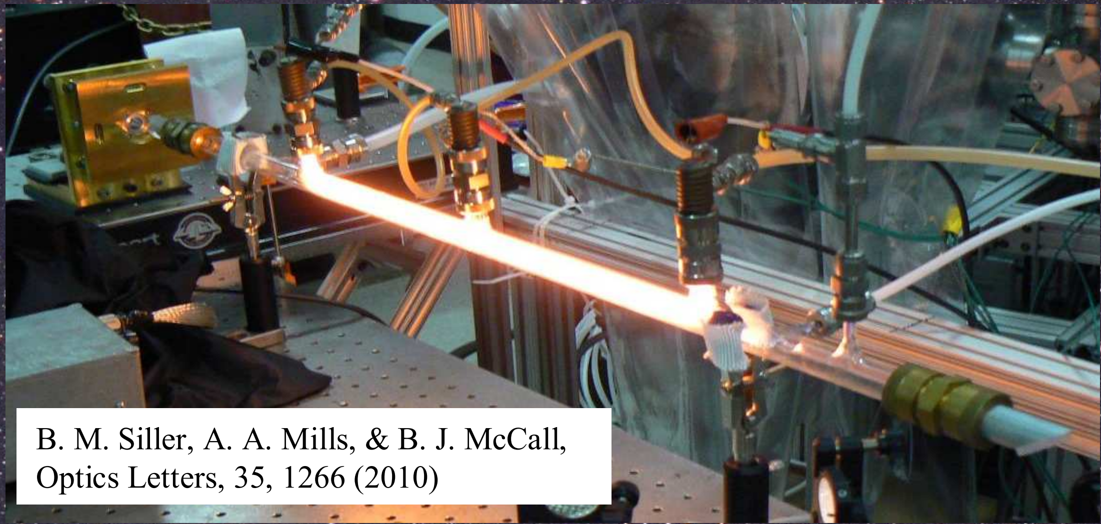
This is our experimental setup; the blue trace is the error signal that tells us how far away the laser is from a cavity resonance

Cavity-Enhanced Velocity Modulation

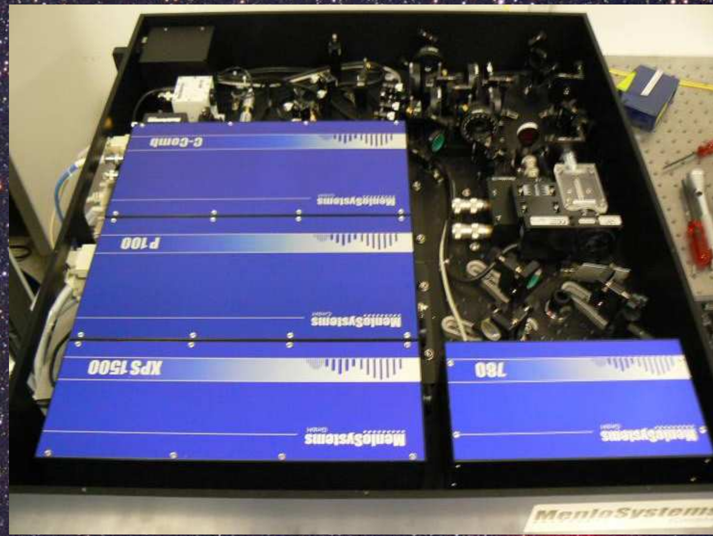


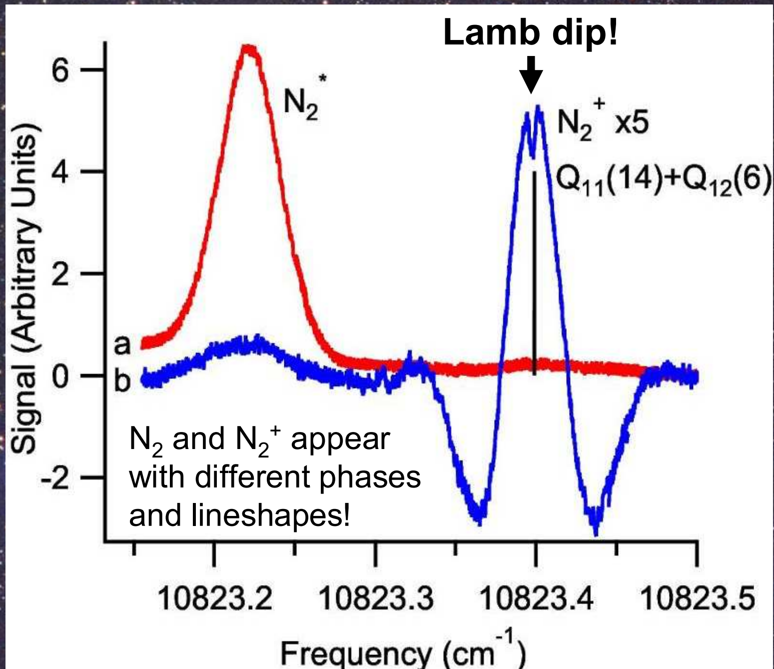
Slow frequency corrections are made using a PZT on the cavity; fast ones using a double-passed AOM.
When the system is locked, the laser always transmits through the cavity (red trace).

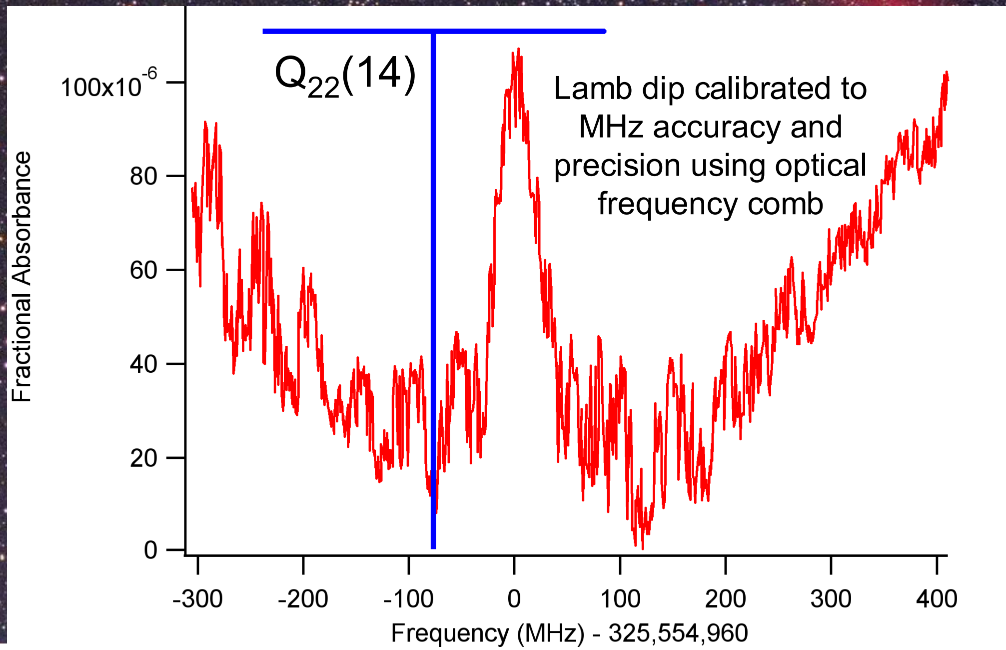
Cavity-Enhanced Velocity Modulation



B. M. Siller, A. A. Mills, & B. J. McCall, Optics Letters, 35, 1266 (2010)



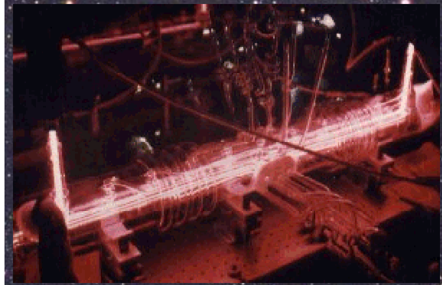




A. A. Mills, B. M. Siller, & B. J. McCall, Chem. Phys. Lett. Frontiers, submitted

Ion Spectroscopy Techniques

We are also developing a new technique that will create a fast ion beam from a supersonic expansion discharge; thereby achieving a physical separation between ions and neutrals while still having a low rotational temperature. Mass spectrometry is also possible simultaneously with this approach.



Oka, Saykally

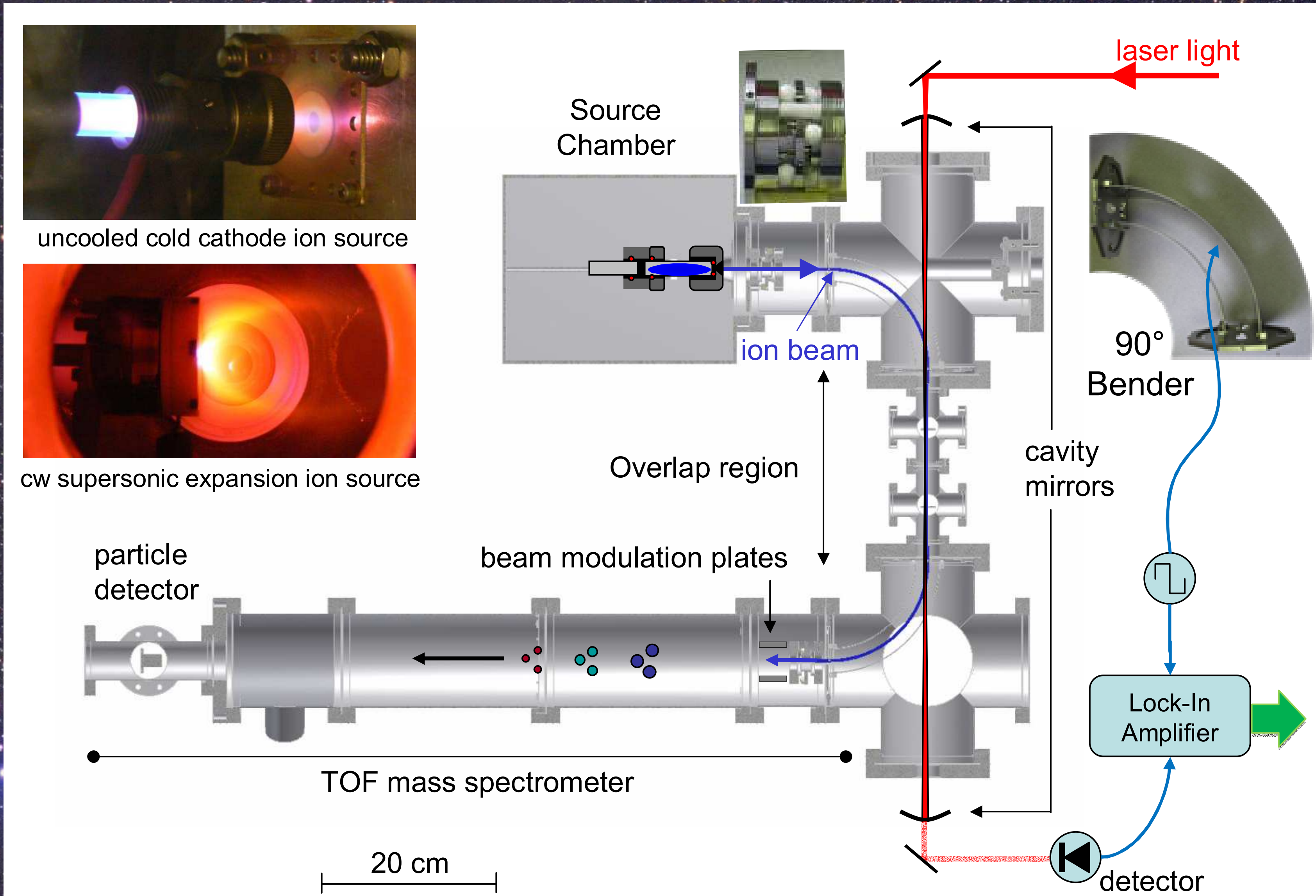
Hirota, Amano

Maier, Nesbitt

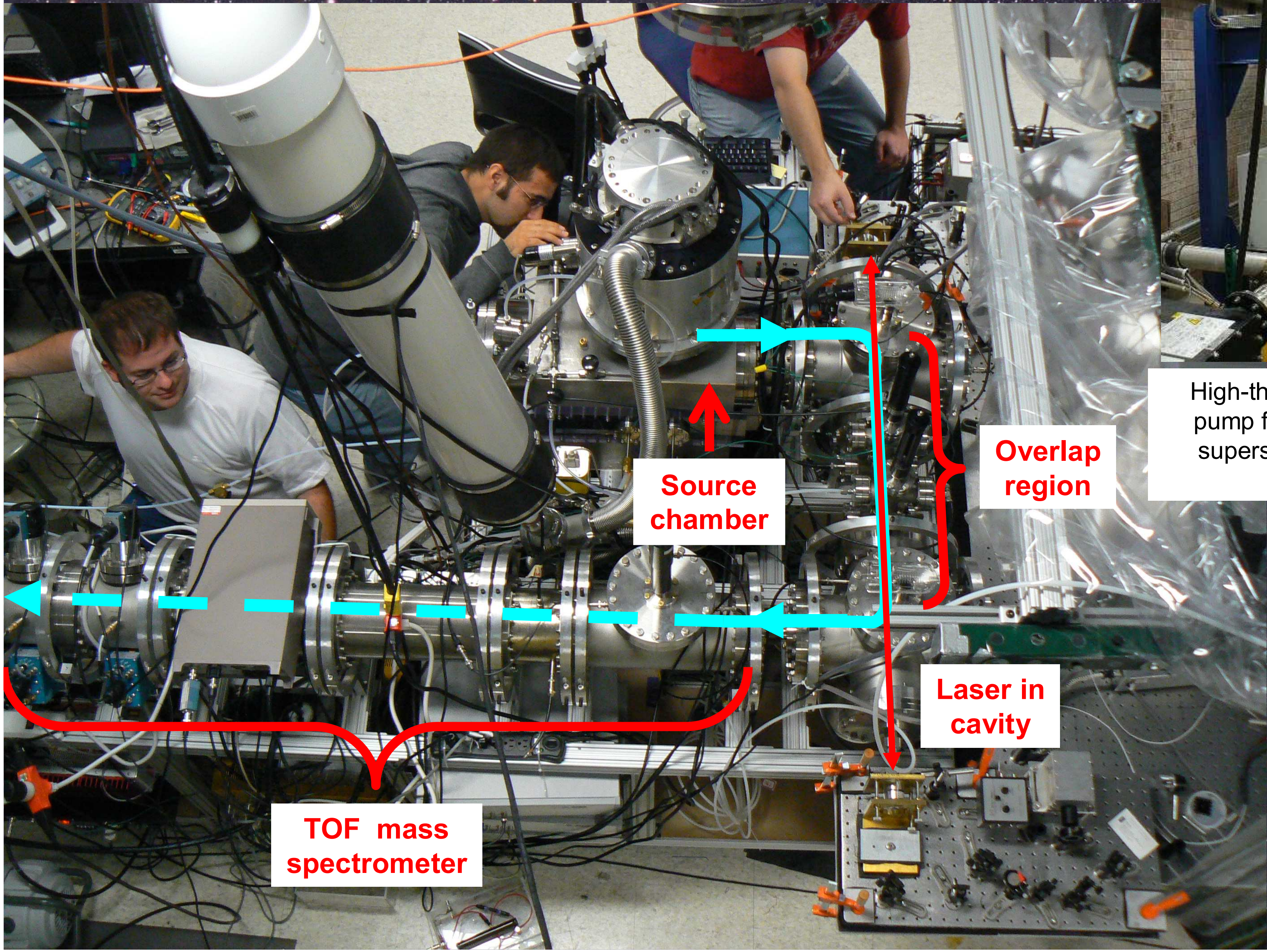
Sensitive
Cooled
Resolved
Ion
BEam
Spectroscopy

	Velocity Modulation	Hollow Cathode	Supersonic Expansion	SCRIBES
High ion column density	✓	✓	✗	✗
Ion-neutral discrimination	✓	✗	✗	✓
Low rotational temperature	✗	✓	✓✓	✓✓
Narrow linewidth	✓✓✓	✓	✓✓	✓✓✓
Compatible with cavity-enhanced spectroscopy	✓	✓	✓	✓
Mass spectrometry of laser-probed ions				✓
Spectral identification of ion mass				✓

SCRIBES Schematic



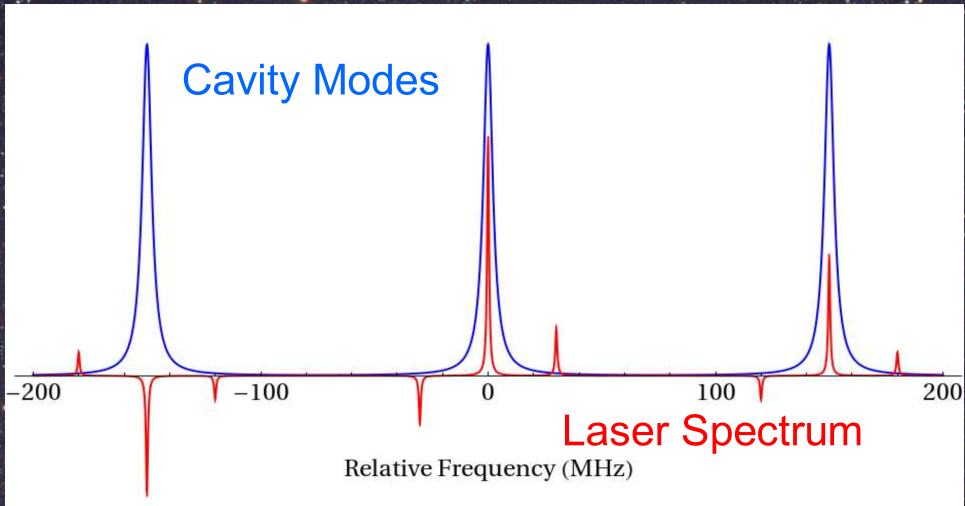
SCRIBES

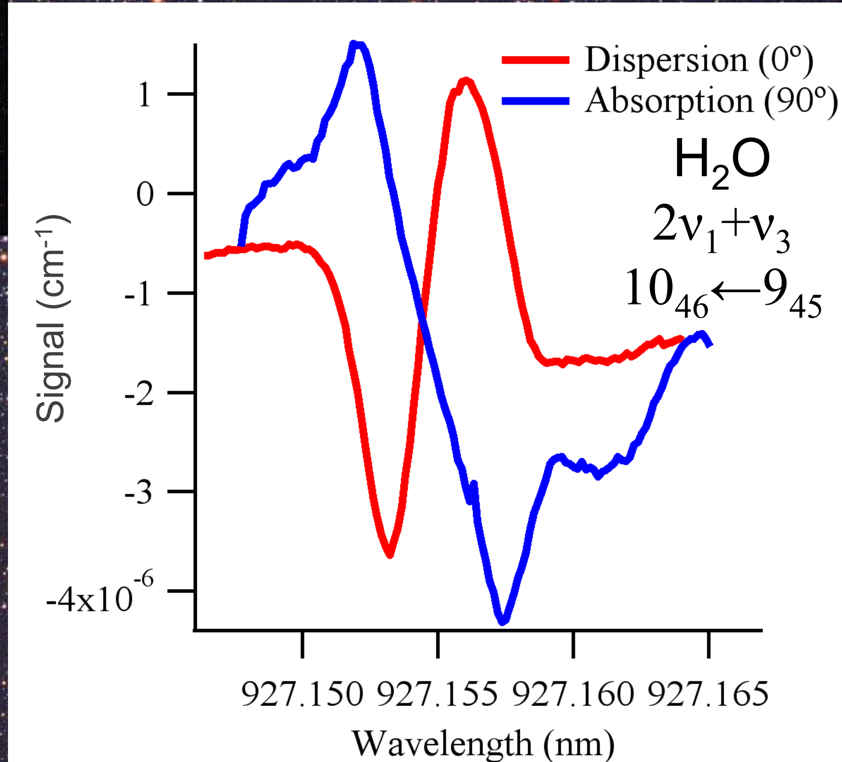


High-throughput Roots pump for future use of supersonic discharge source

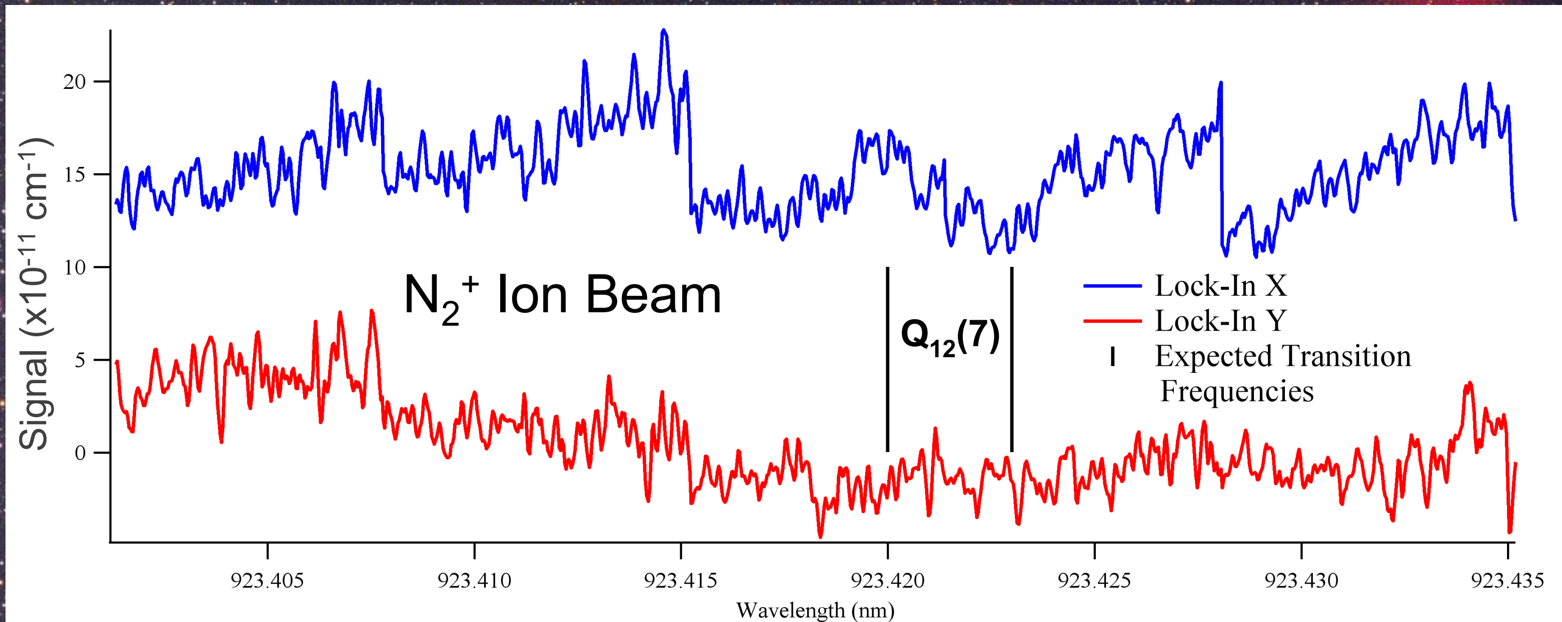
NICE-OHMS

Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy

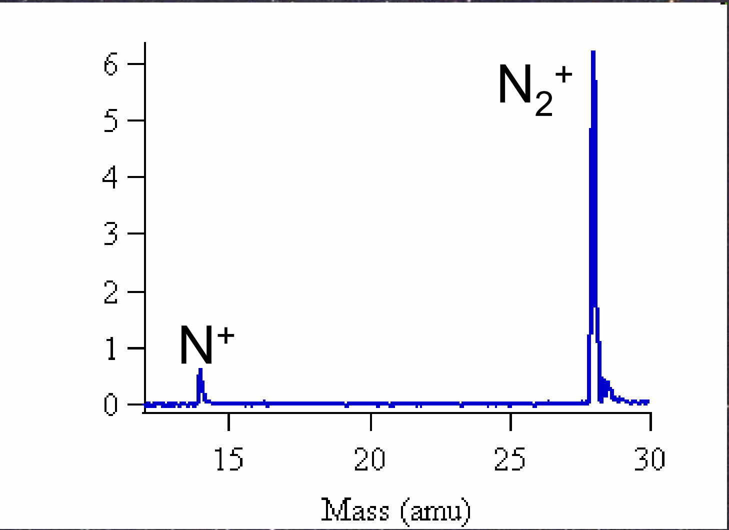




We have used the ultrasensitive technique of NICE-OHMS (Ye & Hall), which combines cavity enhancement and heterodyne modulation, to search for N_2^+ Meinel band absorption in our ion beam, but surprisingly have not seen any signal (expect S/N~100!).

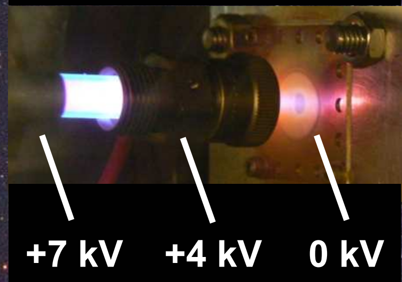


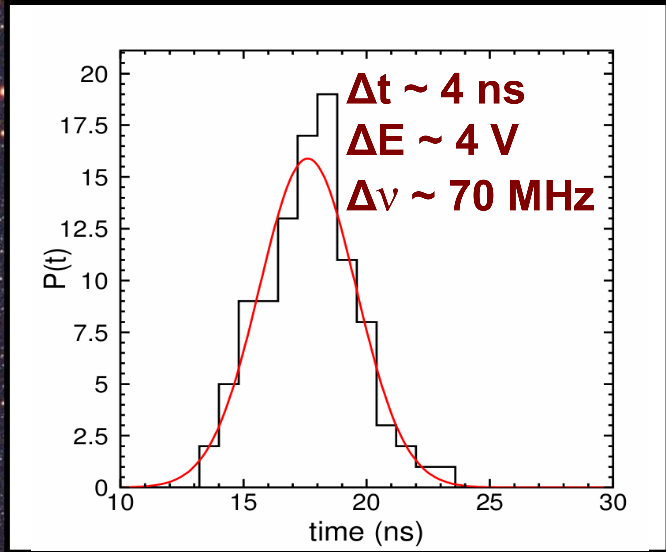
Mass Spectrometry



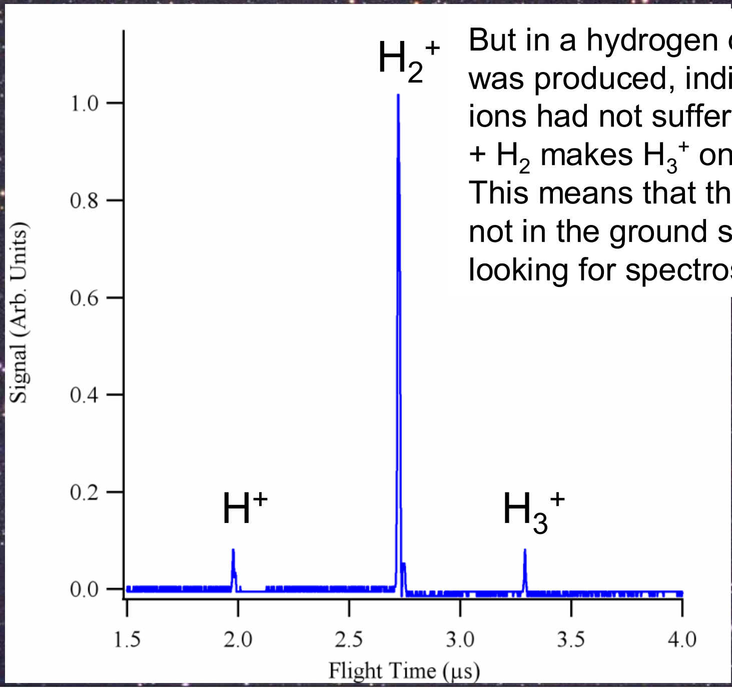
Our original configuration (cathode extraction) yielded a strong N_2^+ beam (left) with narrow energy distribution (right).

Cathode in Front

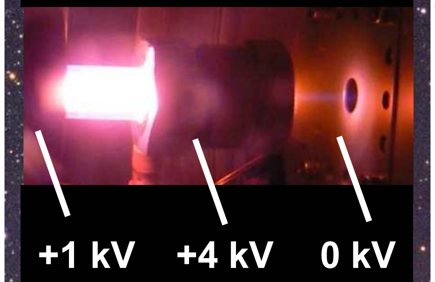




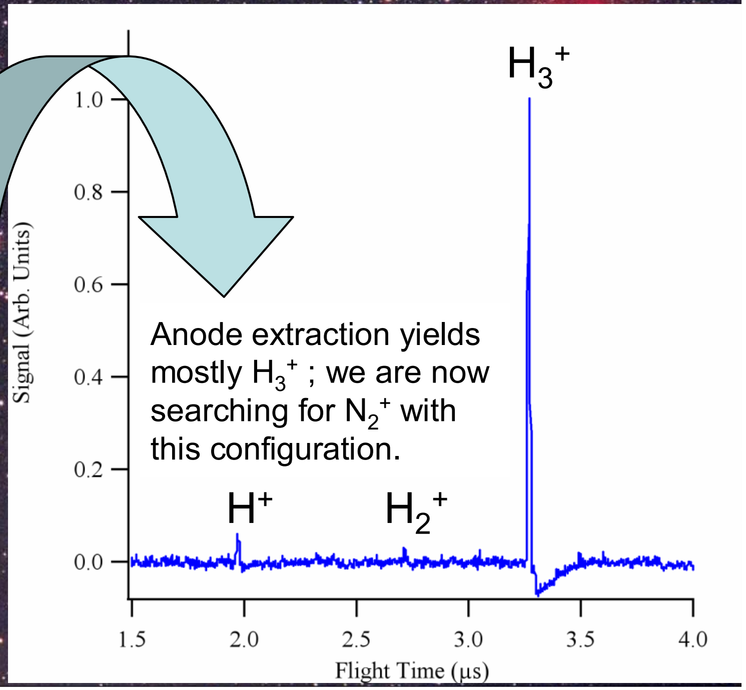
But in a hydrogen discharge, mostly H_2^+ was produced, indicating that extracted ions had not suffered any collisions (H_2^+ + H_2 makes H_3^+ on every collision)! This means that the N_2^+ ions were likely not in the ground state, which we were looking for spectroscopically.



Anode in Front

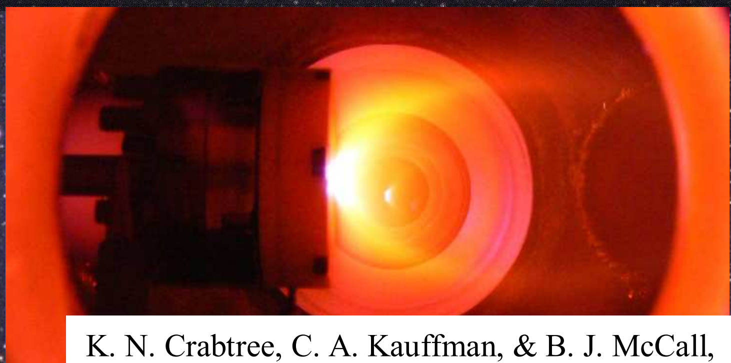


Anode extraction yields mostly H_3^+ ; we are now searching for N_2^+ with this configuration.



The Future of SCRIBES

- N_2^+ spectroscopy
  - initial target for optimization
- Precision IR spectroscopy for Herschel & SOFIA
  - HCO^+, HOC^+, NH^+, …
- Integrate supersonic source
  - CH_5^+, $C_2H_5^+$, …



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