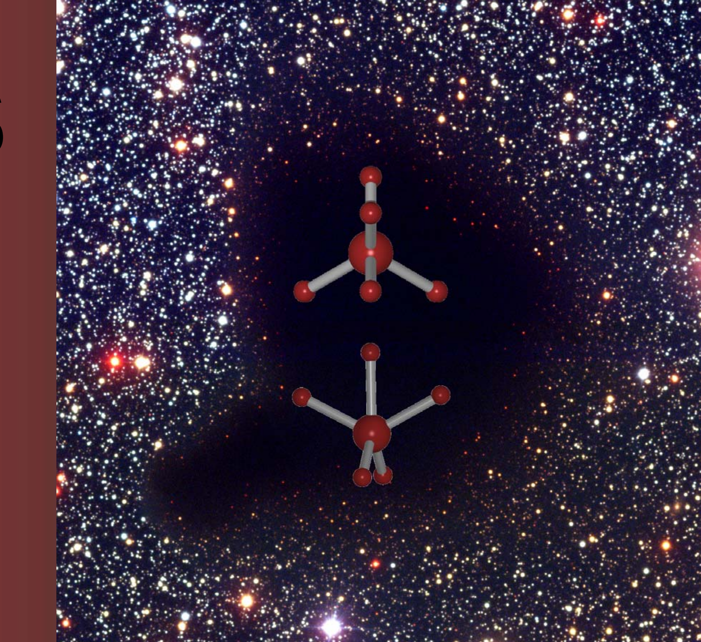
Ultrasensitive Infrared Spectroscopy of Molecular Ions



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Motivations

Why Molecular Ions?

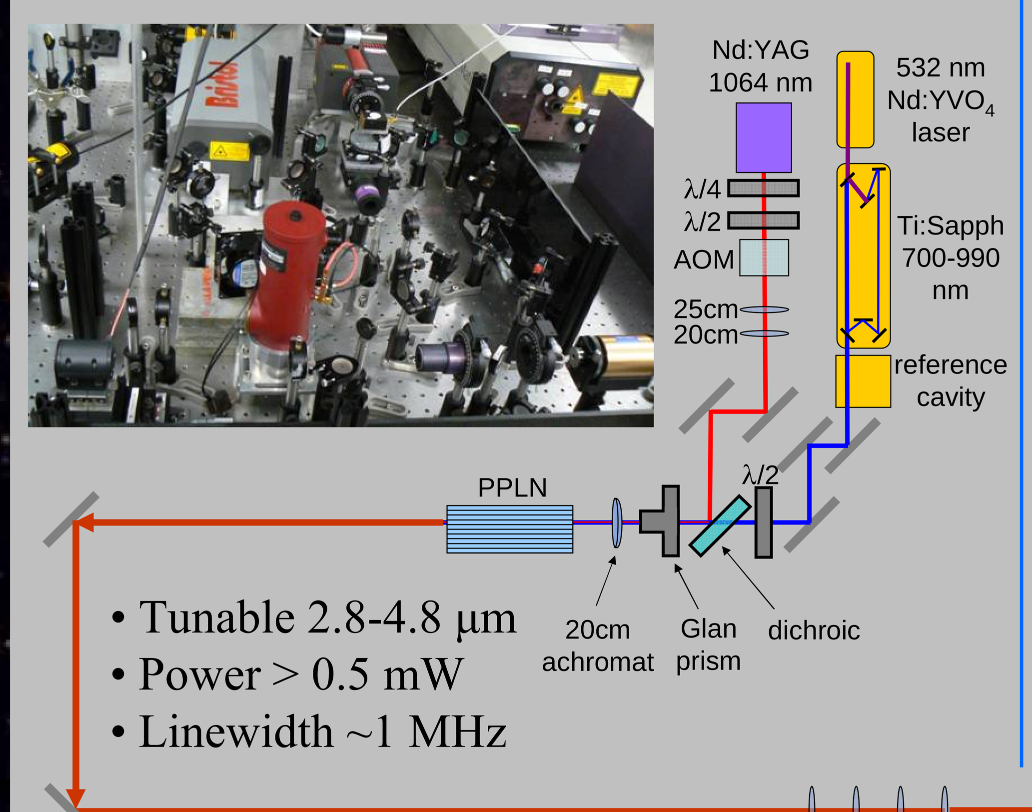
- **Atmospheric Chemistry**: Molecular ions are the key players in the chemical and energetic balance in the ionosphere and auroral regions of Earth's atmosphere and other planetary atmospheres.
- **Combustion**: Molecular ions are potential precursors to soot nucleation, and possible initiators of ignition outside of usual combustion conditions.
- **Propulsion**: Molecular ions represent attractive fuels for ion engines, as well as promising components of new high energy density materials.
- **Astrochemistry**: Molecular ions drive interstellar chemistry.

Why High-Resolution Spectroscopy?

- **Enabling Searches**: Permits searches for molecular ions in the interstellar medium, planetary atmospheres, and combustion environments.
- **Benchmarks for Theory**: Spectroscopy is the gold standard for validating quantum chemical calculations.

Mid-Infrared Laser System

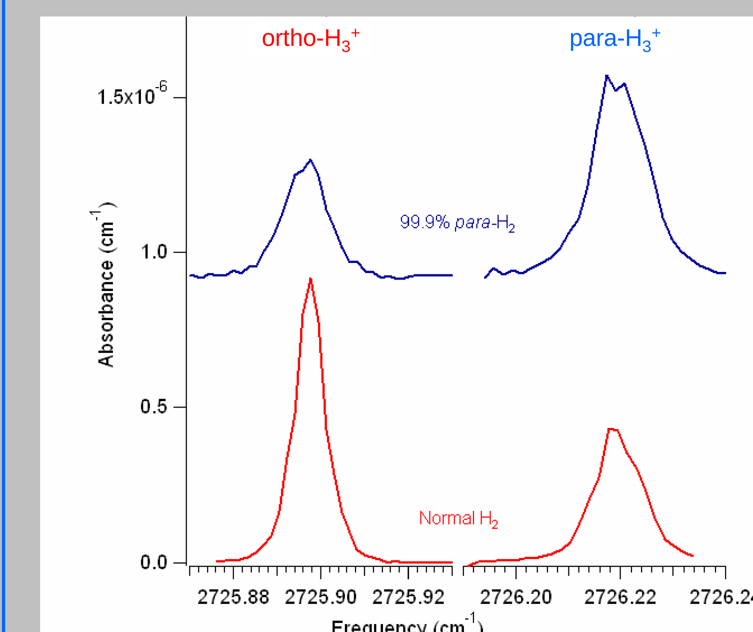
Difference Frequency Generation



- Tunable 2.8-4.8 μm
- Power > 0.5 mW
- Linewidth ~1 MHz

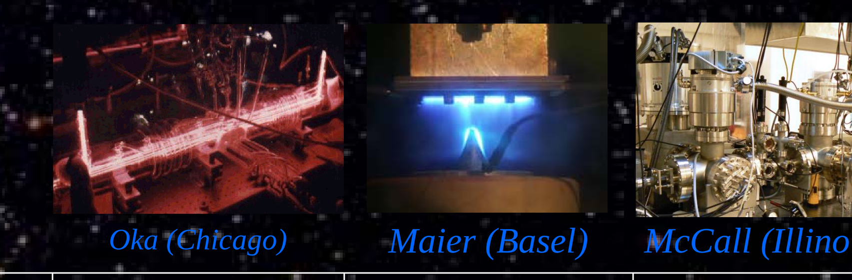
Initial Spectroscopic Results

Cavity ringdown spectra of H_3^+ in a supersonic expansion discharge source.



Comparison with Other Techniques

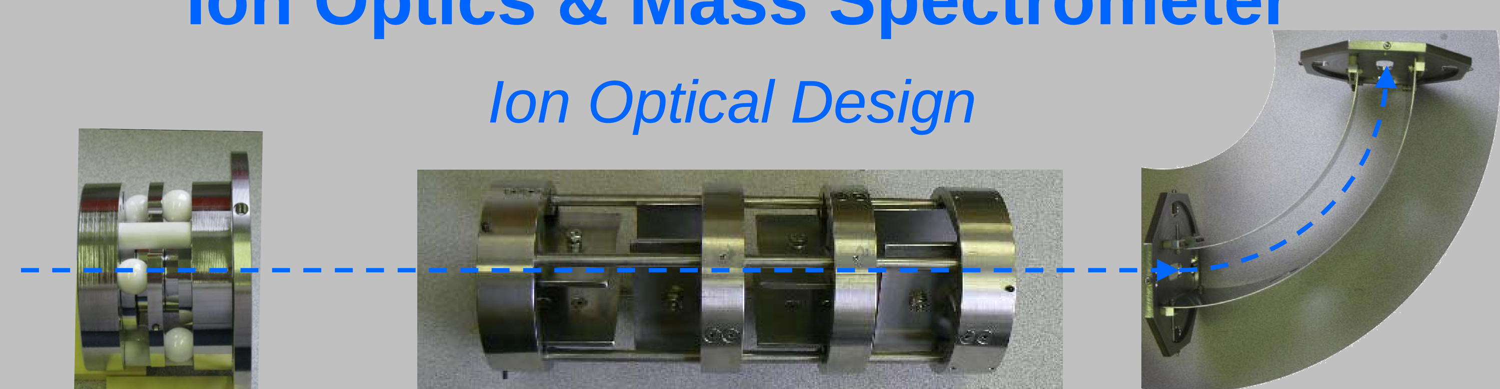
Two techniques have been widely used for molecular ion spectroscopy, but both have inherent limitations.



	Velocity Modulation	Supersonic Expansion	SCRIBES
High ion column density	✓		
Ion-neutral discrimination	✓		✓
Low rotational temperature		✓	✓
Sub-Doppler linewidth		✓	✓
Ultra-narrow linewidth (kinematic compression)			✓
Compatible with cavity-enhanced spectroscopy		✓	✓
Mass spectrometry of laser-probed ions			✓
Spectral identification of ion mass			✓

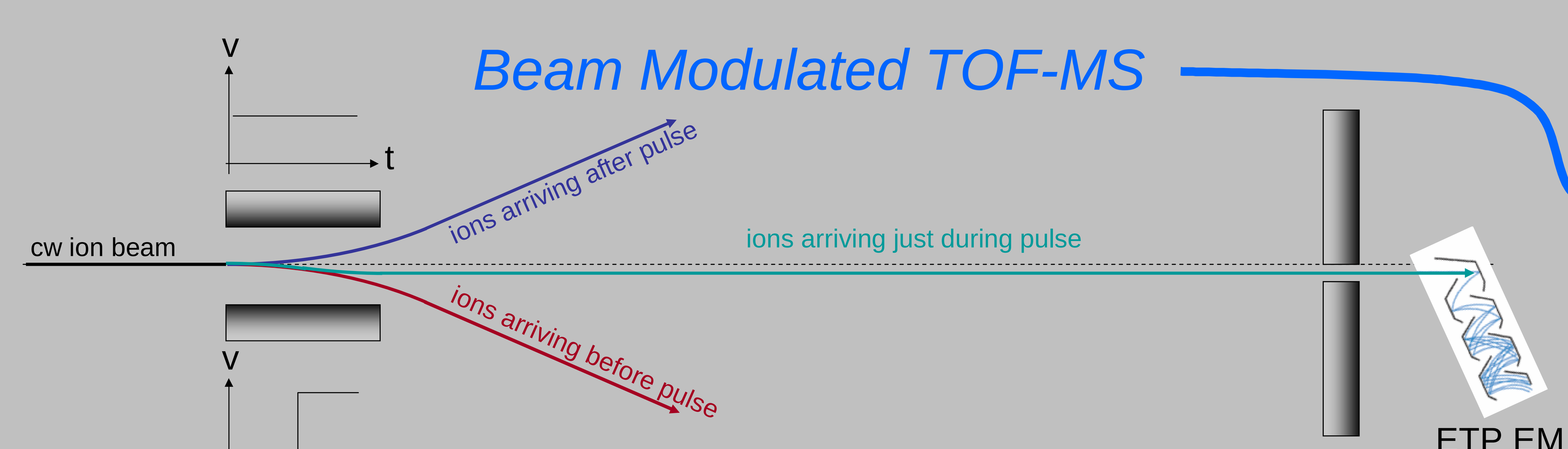
Ion Optics & Mass Spectrometer

Ion Optical Design



An Einzel lens is used to focus the ion beam from the source… …then the beam is steered and "walked" using a set of deflector plates… …and a cylindrical bender turns it to overlap with the laser.

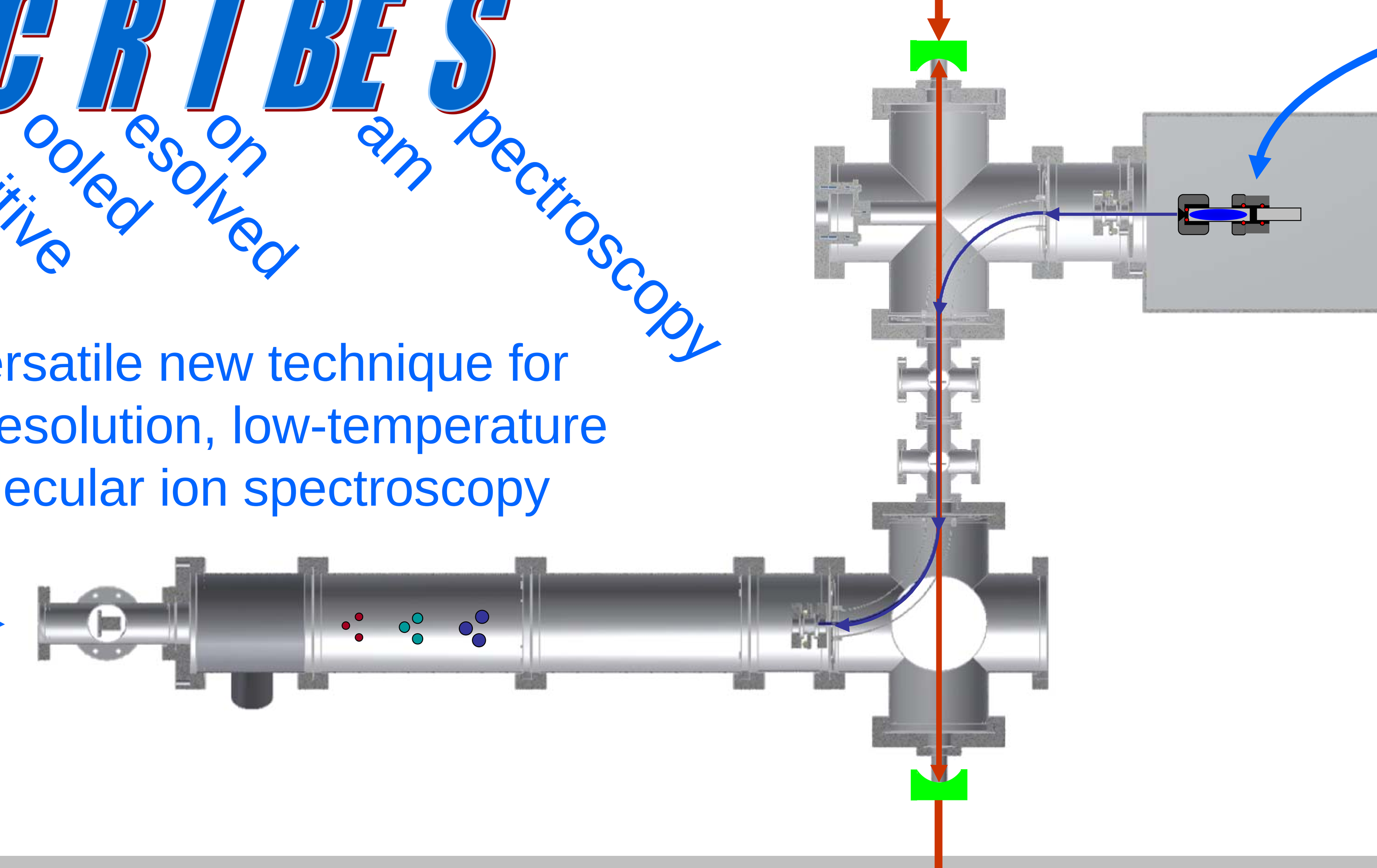
Beam Modulated TOF-MS



SCRIBES

Sensitive **C**ooled **R**esolved **I**on **BE**am **S**pectroscopy

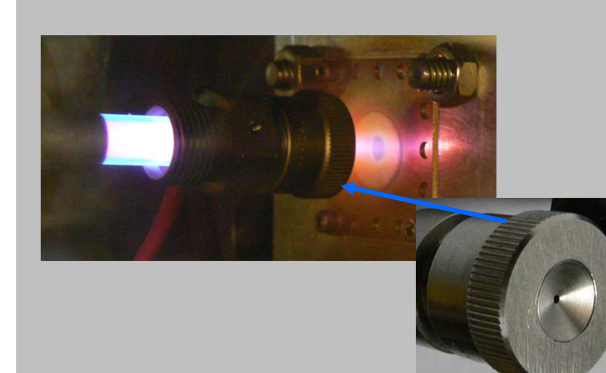
A versatile new technique for high-resolution, low-temperature molecular ion spectroscopy



Molecular Ion Sources

Cold Cathode

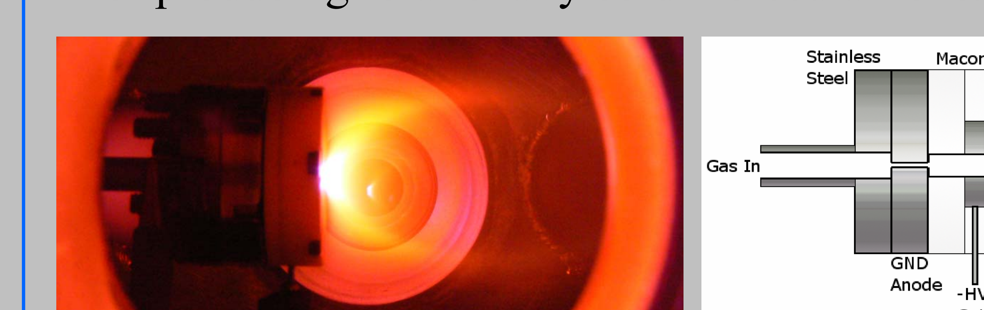
Our initial test source is an uncooled cold cathode (adapted from a Saykally group design).

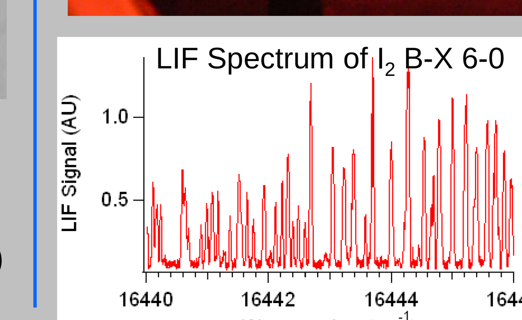


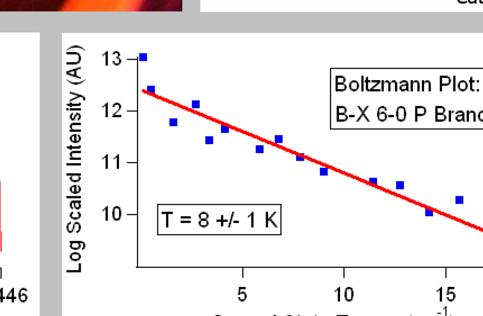
- Discharge current: ~1 mA
- Emission current: ~50 μA
- Beam current: ~1.5 μA (N_2^+)
- Nozzle: 1 mm ϕ, Pierce

Supersonic Expansion Discharge

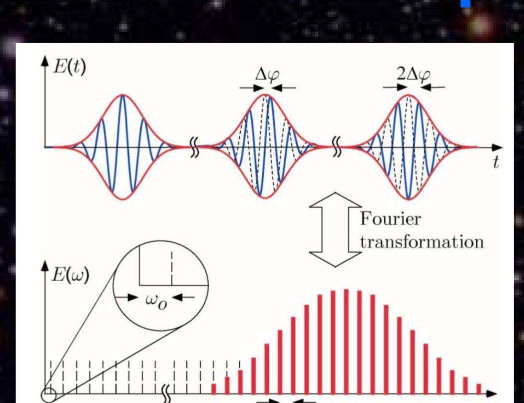
We are also developing and characterizing a continuous supersonic expansion discharge source for producing rotationally cold molecular ions.



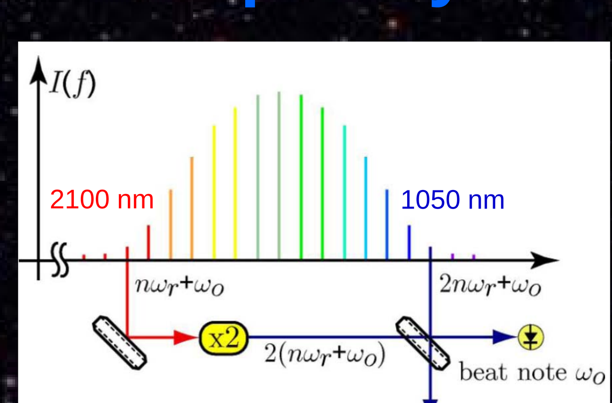




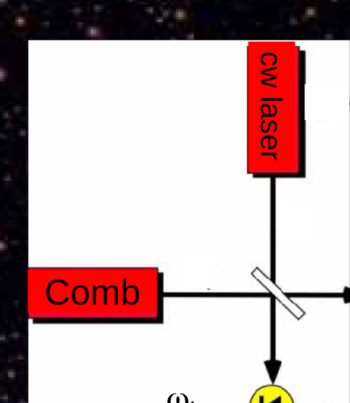
Optical Frequency Comb



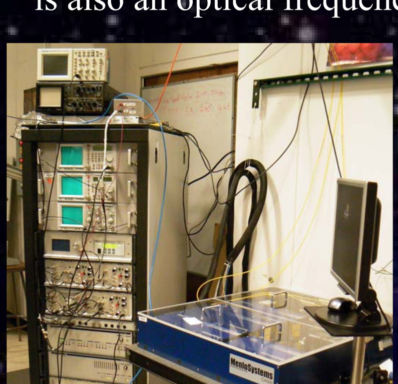
A pulse train of a stabilized fs laser is also an optical frequency comb.



Doubling the comb, and beating the two combs, yields the offset frequency.



Beating the comb with a cw laser yields a beat frequency.



MenloSystems FC1500

$$\omega_{Ti} = n_{Ti}\cdot\omega_{rep} + 2\omega_{offset} + \omega_{Ti,beat}$$

$$-\ [\omega_{YAG} = n_{YAG}\cdot\omega_{rep} + \omega_{offset} + \omega_{YAG,beat}]$$

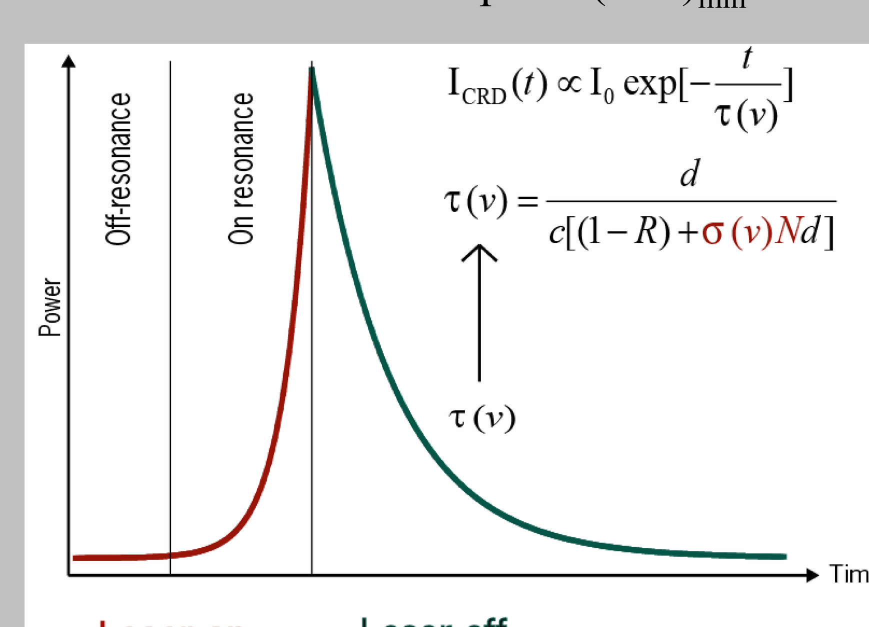
$$= \omega_{DFG} = (n_{Ti} - n_{YAG})\,\omega_{rep} + \omega_{offset} + (\omega_{Ti,beat} - \omega_{YAG,beat})$$

integer ~800,000 | 100 MHz ±1 mHz | ~20 MHz ±2 Hz | ~10 MHz ±50 kHz

Spectroscopic Techniques

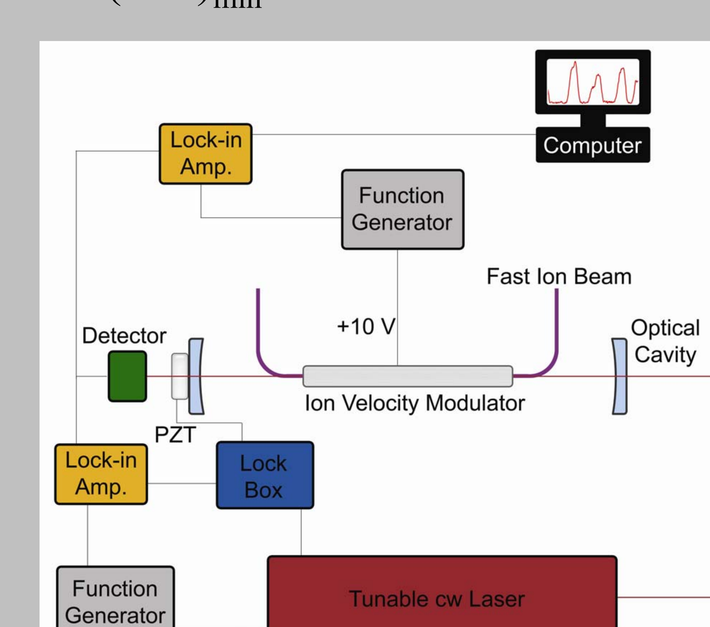
Continuous-Wave Cavity Ringdown

- Easy to implement (AOM, comparator)
- Min. detectable absorption $(\Delta I/I)_{min} \sim 10^{-7}$



Cavity Enhanced Beam Velocity Modulation

- More involved (locking loop)
- $(\Delta I/I)_{min} \sim 10^{-7}$ / Finesse

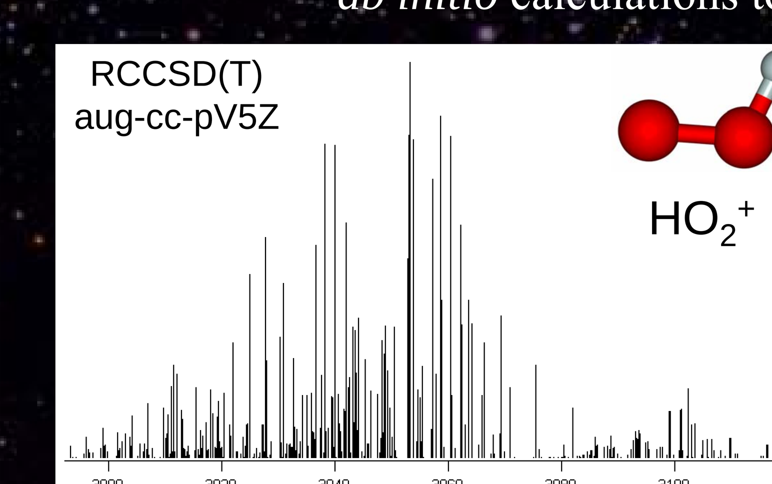


Target Molecular Ions

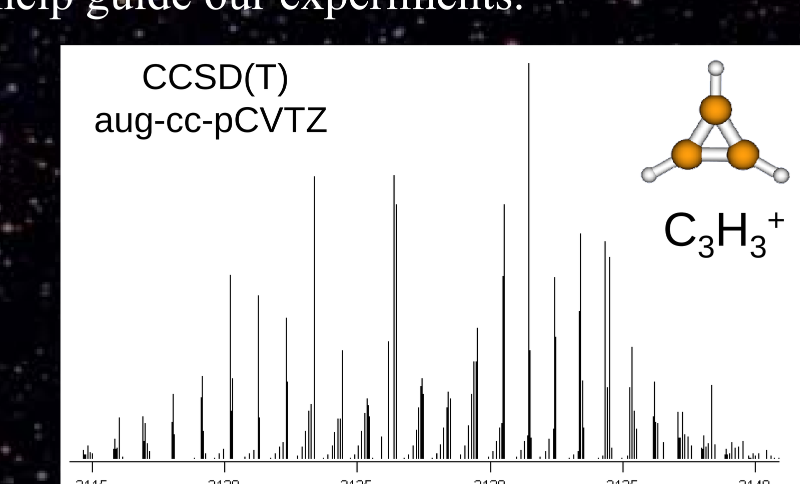
We plan to study larger and more complex ions than can be studied in hot plasmas, including N_5^+, $H_2O_2^+$, CH_5^+, $C_2H_5^+$, $C_3H_3^+$, and $C_6H_7^+$. We welcome input on what will be the best targets for supporting the Air Force mission!

Theoretical Support

We have been collaborating with theorists to perform high-level *ab initio* calculations to help guide our experiments.



Widicus Weaver, Woon, Ruscic, McCall, *Astrophys. J.* **697**, 601 (2009)



Mills, A. Perera, R. Bartlett, McCall, in prep