# A Continuous Supersonic Expansion Discharge Source for High-Precision Mid-Infrared Spectroscopy of Cold Molecular Ions

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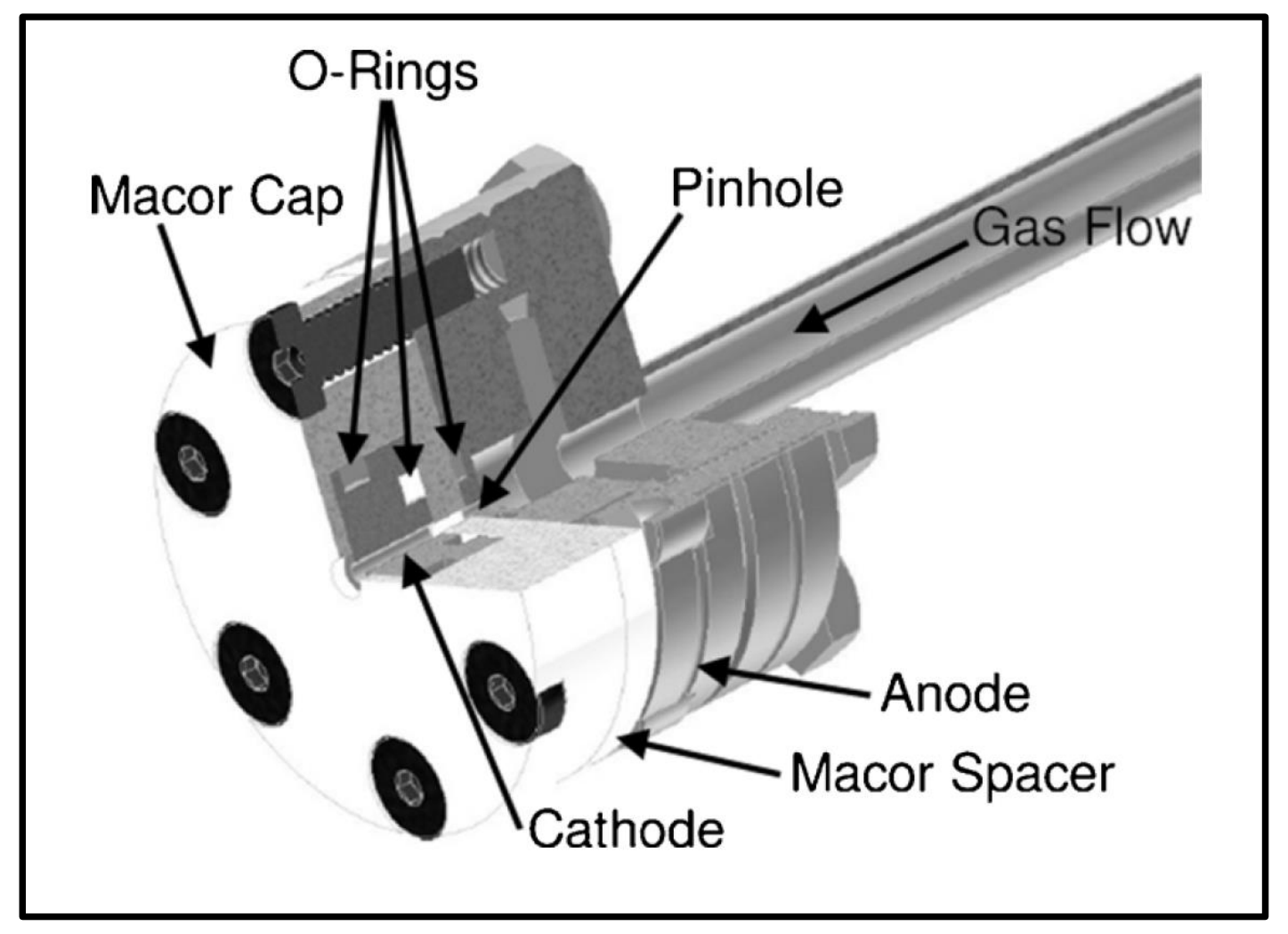
## Background

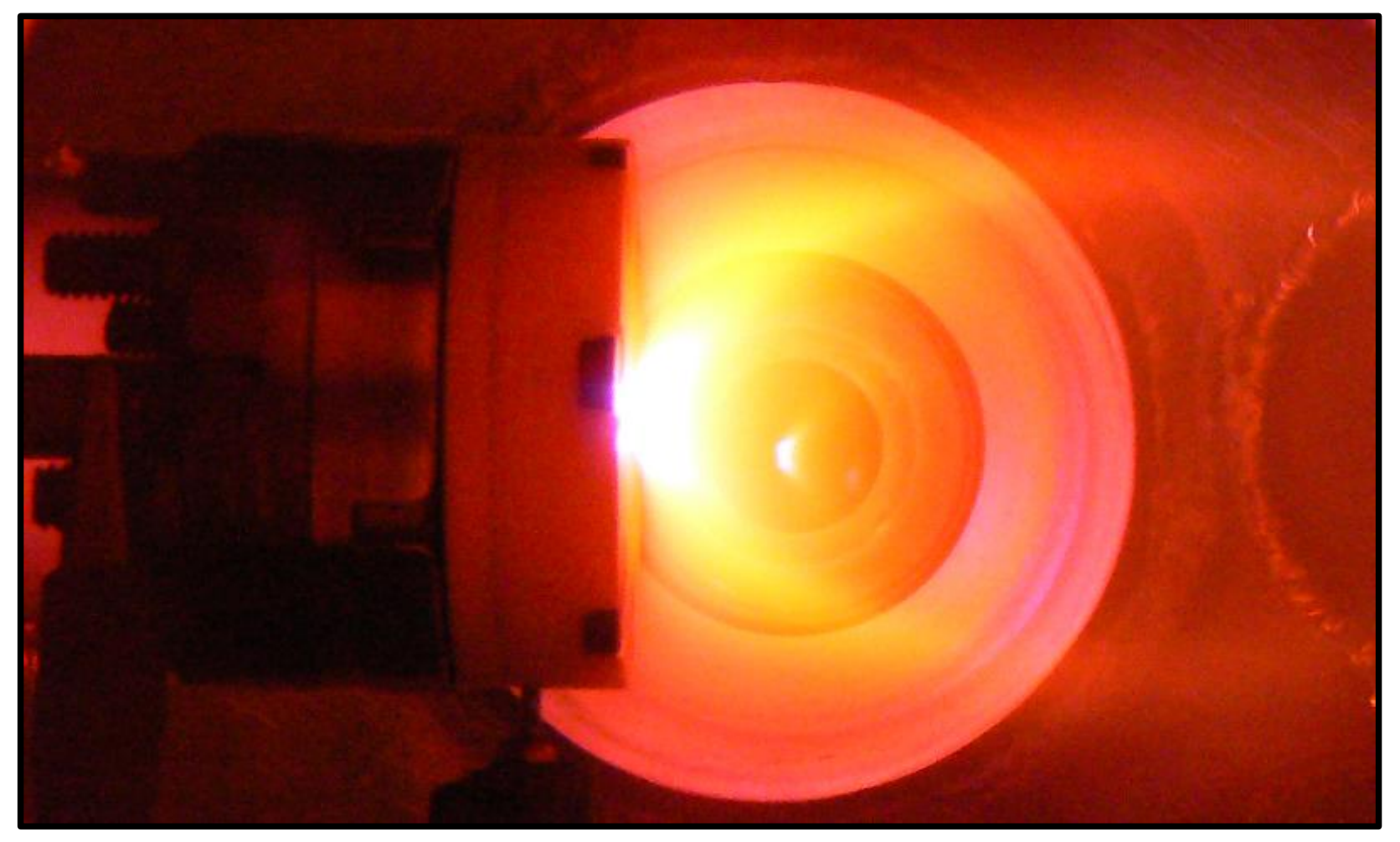
The low temperatures and pressures of the interstellar medium provide an ideal environment for the long-lived existence of molecular ions that play an essential role in the chemistry of the universe. There is a need for high-precision spectra to facilitate new astronomical discoveries and provide a deeper understanding of interstellar chemistry, but forming ions in measurable quantities in the laboratory has proved challenging. Typical discharge cells, even when cryogenically cooled, lead to diluted and congested spectra from which extracting chemical information is difficult. Here we overcome this challenge by coupling an electric discharge to a continuous supersonic expansion to form ions cooled to low temperatures.

## Supersonic Source Design

As high pressure gas exits the nozzle it adiabatically expands into a vacuum which leads to cooling of the gas. Incorporating a high-voltage discharge into this design has allowed for the formation of high densities of ions ($10^{10} – 10^{12}$ $cm^{-3}$ for $H_3^+$) that quickly cool upon leaving the throat of the nozzle. To form an effective supersonic expansion the gas must be quickly pumped out of the vacuum chamber. To this end we employ a Leybold roots blower system capable of an evacuation rate of 13,000 $m^3$/hr.



The geometry of the source has been optimized previously , with the modular design chosen for easy replacement of parts in the case of failure.



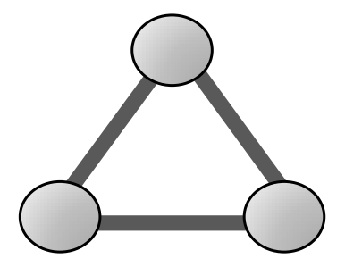
The source producing a jet of nitrogen plasma.

K. N. Crabtree, C. A. Kaufman, and B. J. McCall, *Rev. Sci. Instrum*. **81**, 086103 (2010).

## Ion Targets

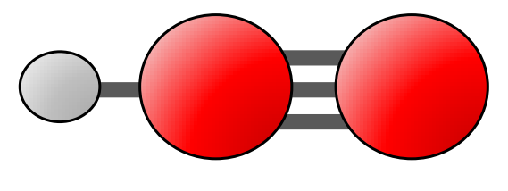
Due to the low density of the molecular beam, ions produced by the source experience very few ion-molecular interactions. This makes the source distinctively suited for the study of primary ions such as $H_2CO^+$. In working toward this ultimate goal, several less-complex ions have been (and will be) studied to characterize the abilities of the source.

$H_3^+$



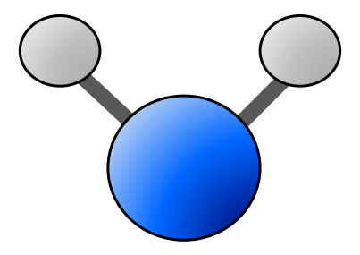
$H_2 + H_2^+ \rightarrow H_3^+ + H$

$HN_2^+$



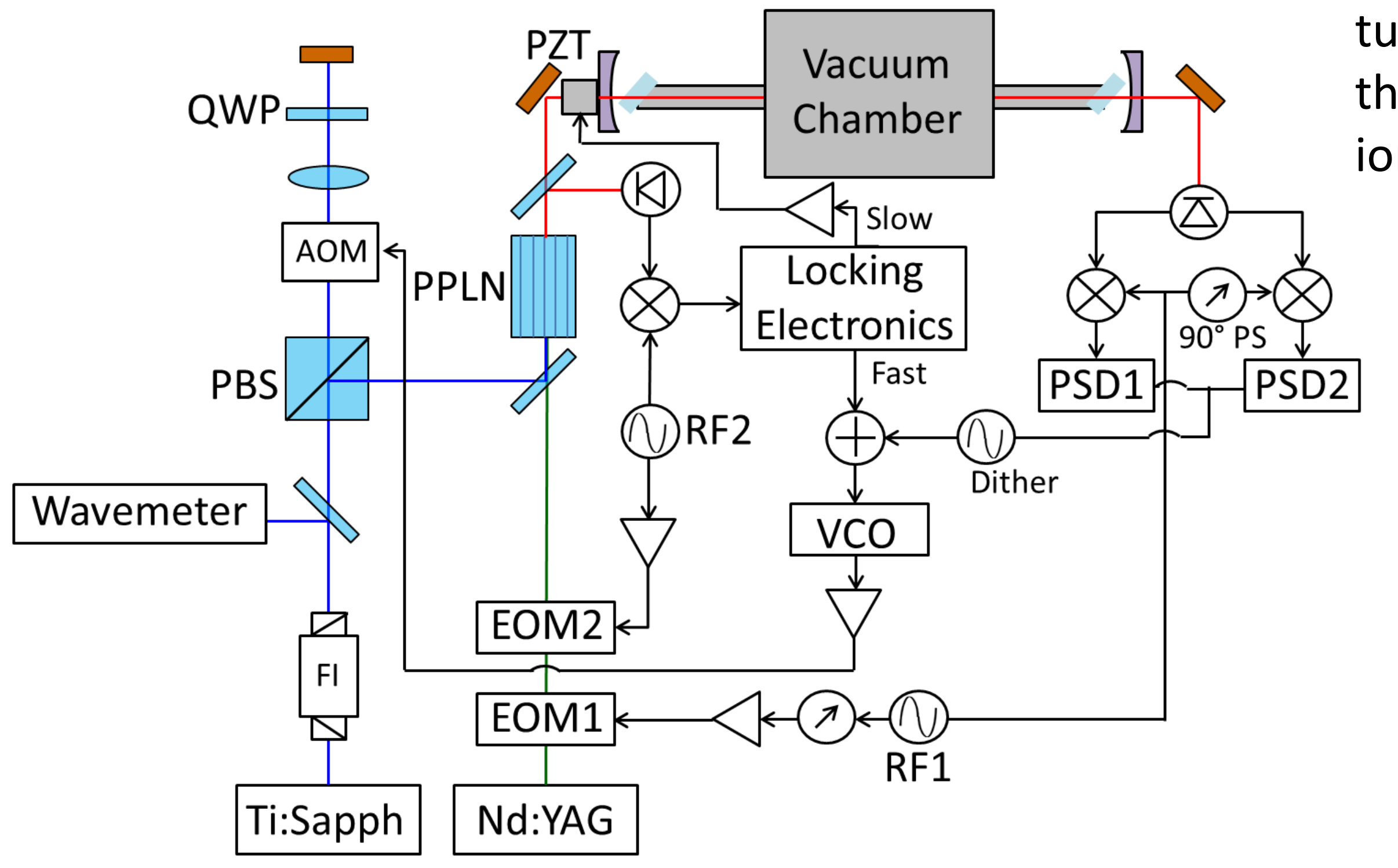
$H_3^+ + N_2 \rightarrow HN_2^+ + H_2$

$H_2O^+$



A primary ion

## High-Precision Spectroscopy



A schematic of the DFG-based mid-IR NICE-OHMS instrument

Noise-immune cavity-enhanced optical heterodyne spectroscopy (NICE-OHMS) is used in combination with a widely tunable mid-Infrared light source based on difference frequency generation (DFG) to probe ions from 3-5 µm. Using this spectrometer in combination with an optical frequency comb will allow for rovibrational transitions of primary ions to be determined to a precision of 1 MHz.

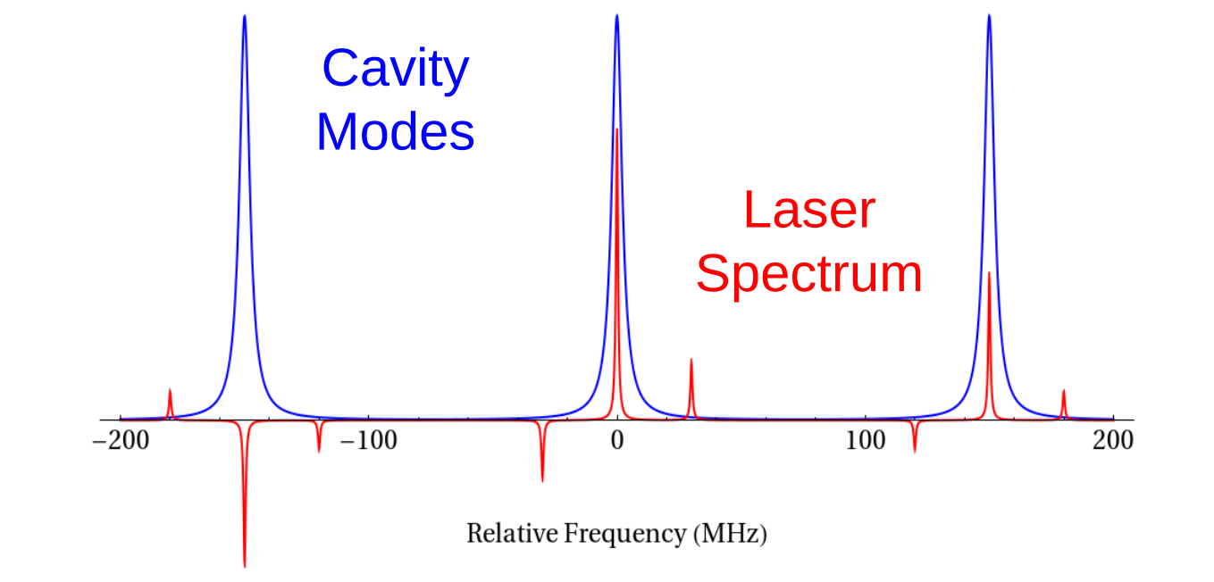
### Light Source: DFG

Widely tunable light generated in a non-linear crystal

- Fixed wavelength Nd:YAG (1064 nm)
- Tunable Ti:Sapphire (800-1100 nm)
- Capable of producing 3-5 µm light by depending on crystal channel and temperature
- 140-200 µW of power

### Noise-Immune

In cavity-enhanced techniques, frequency fluctuations in the light source are converted to variations in intensity that generate noise in the signal. The heterodyne nature of NICE-OHMS allows the technique to be immune to these frequency jitters and attain a higher level of sensitivity.



To achieve noise immunity the heterodyne frequency is matched to the FSR of the cavity. In the presence of an absorber the sidebands do not cancel and a signal is detected at the heterodyne frequency.

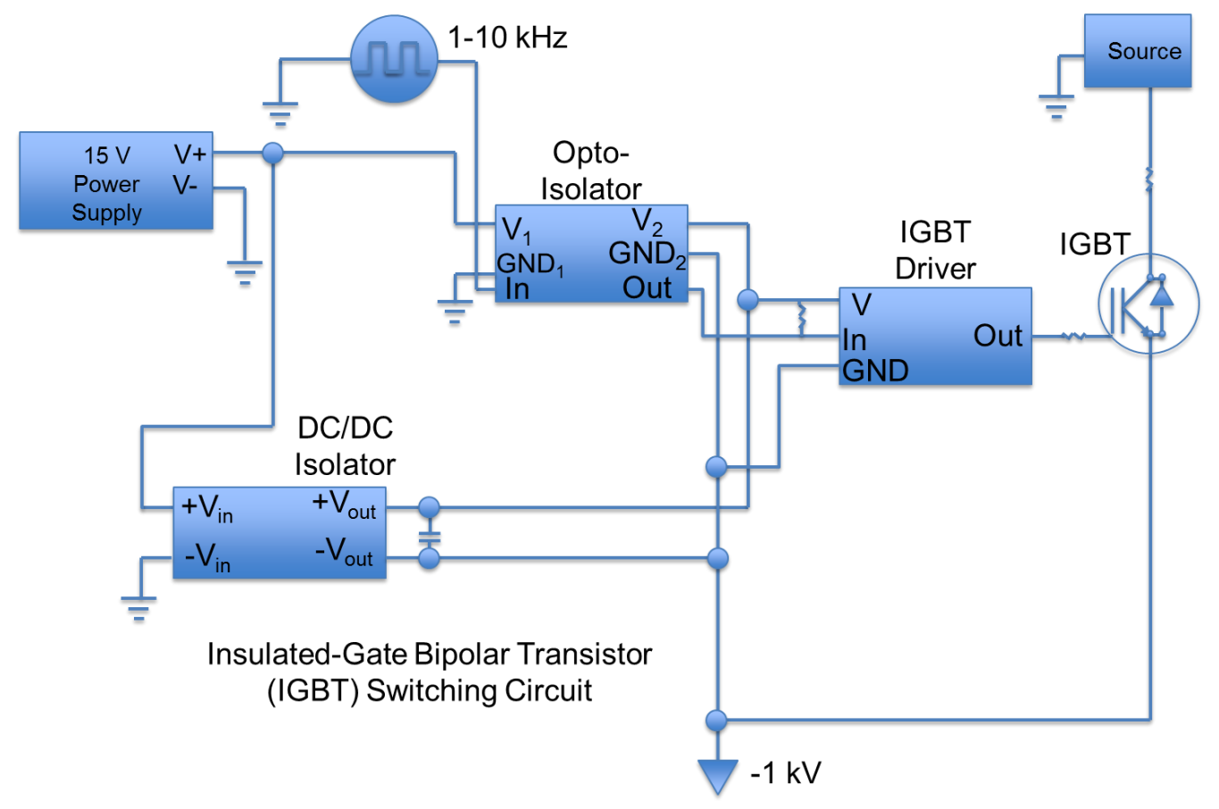
### Cavity-Enhanced

The path length is increased due to numerous passes through the sample, but light is only coupled into the cavity when equal to an integer multiple of the free spectral range (FSR).

- Builds up power
- Must match frequency of light to cavity!
- Piezo used to make slow corrections to length of cavity (70 Hz)
- Voltage controlled oscillator (VCO) for fast corrections to Ti:Sapphire laser via a double-pass acoustic optic modulator (AOM) set-up

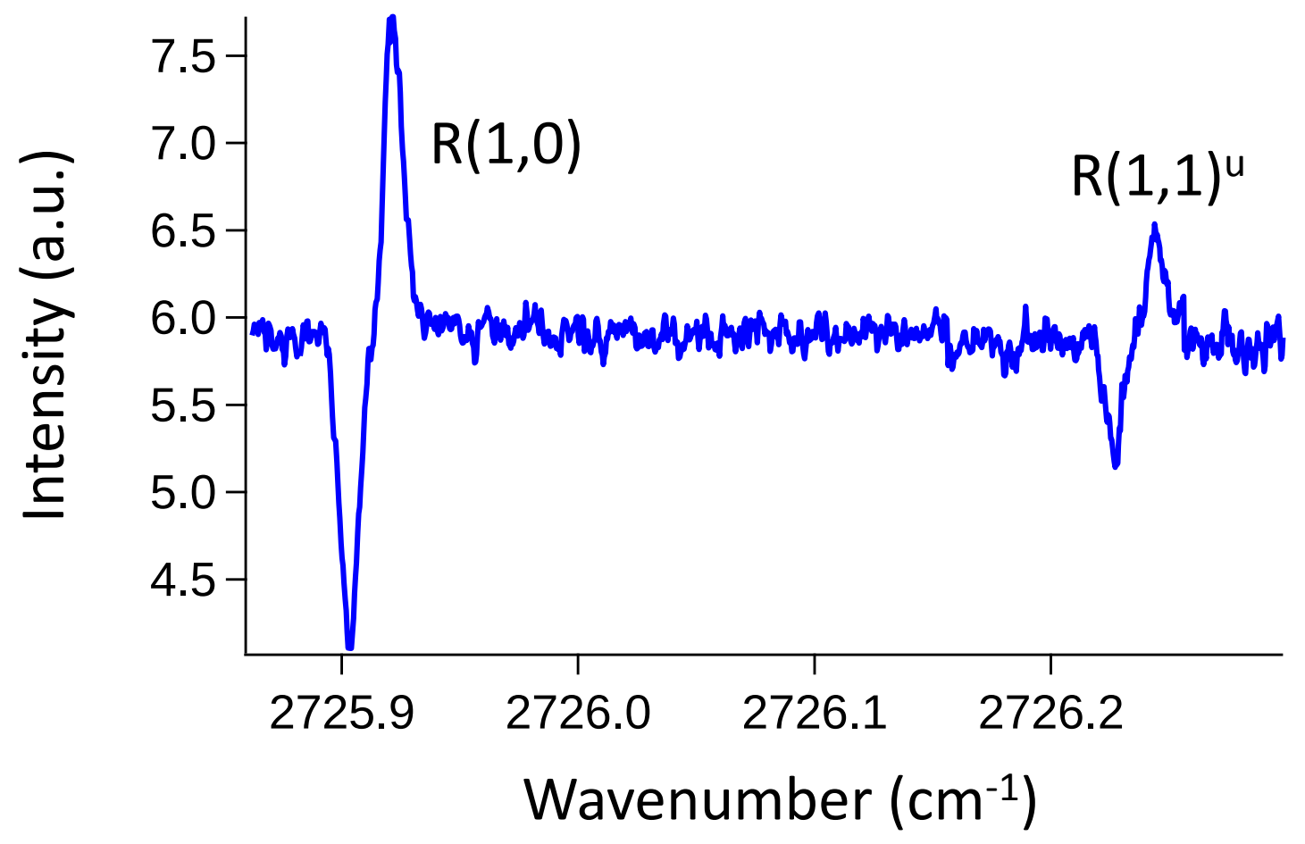
### Another Layer of Modulation

A custom high-voltage circuit is used to modulate the discharge from 50 Hz – 80 kHz.



Insulated-Gate Bipolar Transistor (IGBT) Switching Circuit

## Results

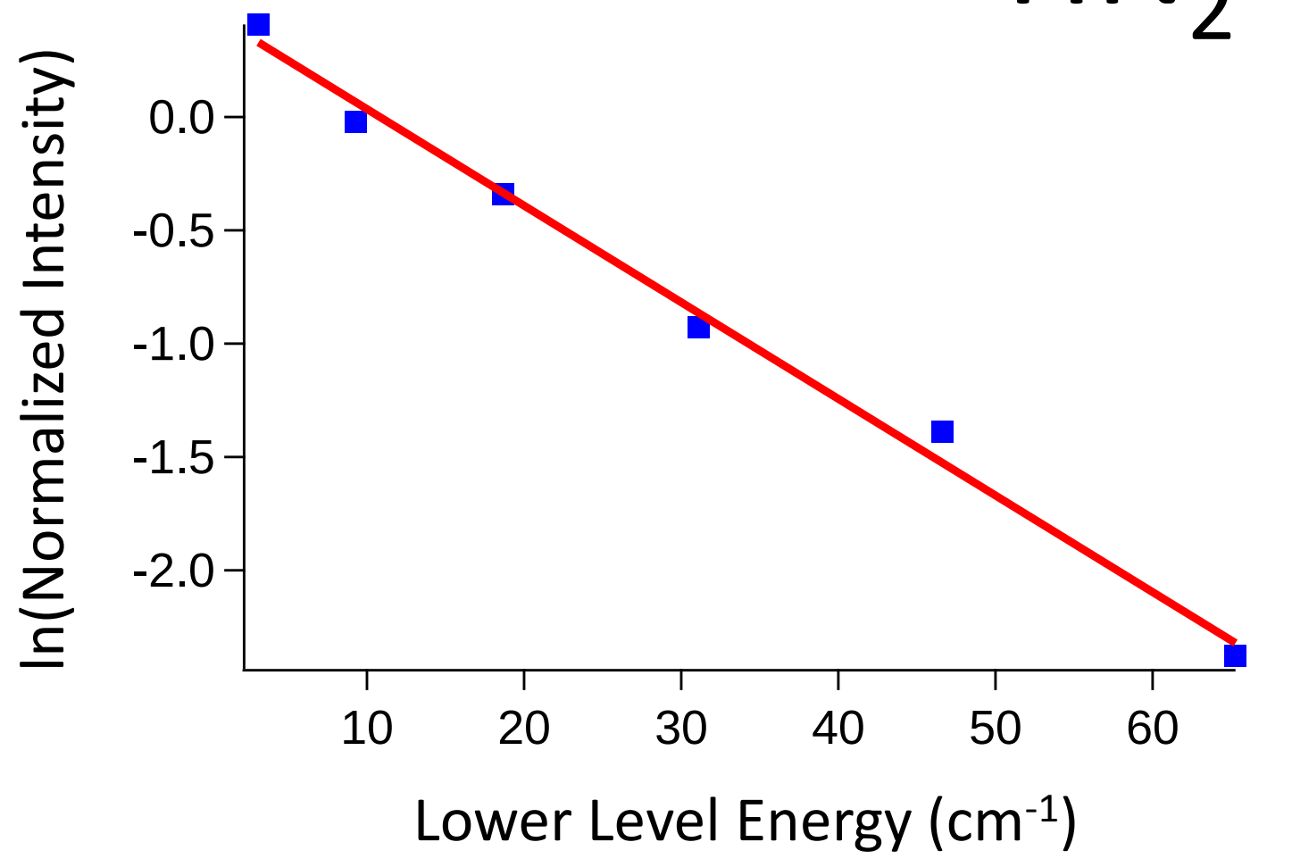


Due to their close proximity in frequency space, the relative intensities of the R(1,0) and $R(1,1)^u$ transitions are used to estimate a rotational temperature for $H_3^+$, which is then further verified through a Boltzmann analysis.

$H_3^+$: 80 – 120 K

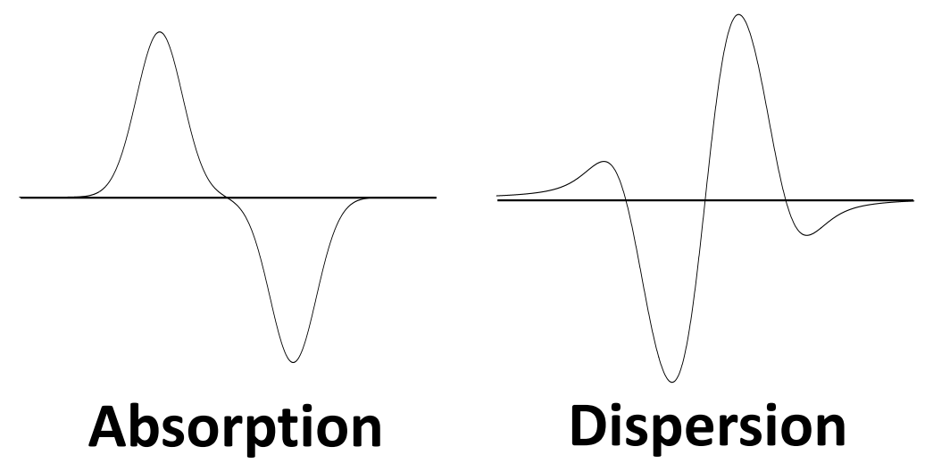
With a small rotational constant $HN_2^+$ is a reliable measure of the cooling abilities of the source. Performing a Boltzmann analysis of the J = 0-6 transitions of the $v_1$ fundamental band of $HN_2^+$ gives a temperature that is in good agreement with previous studies of this ion.

$HN_2^+$: 35 – 40 K

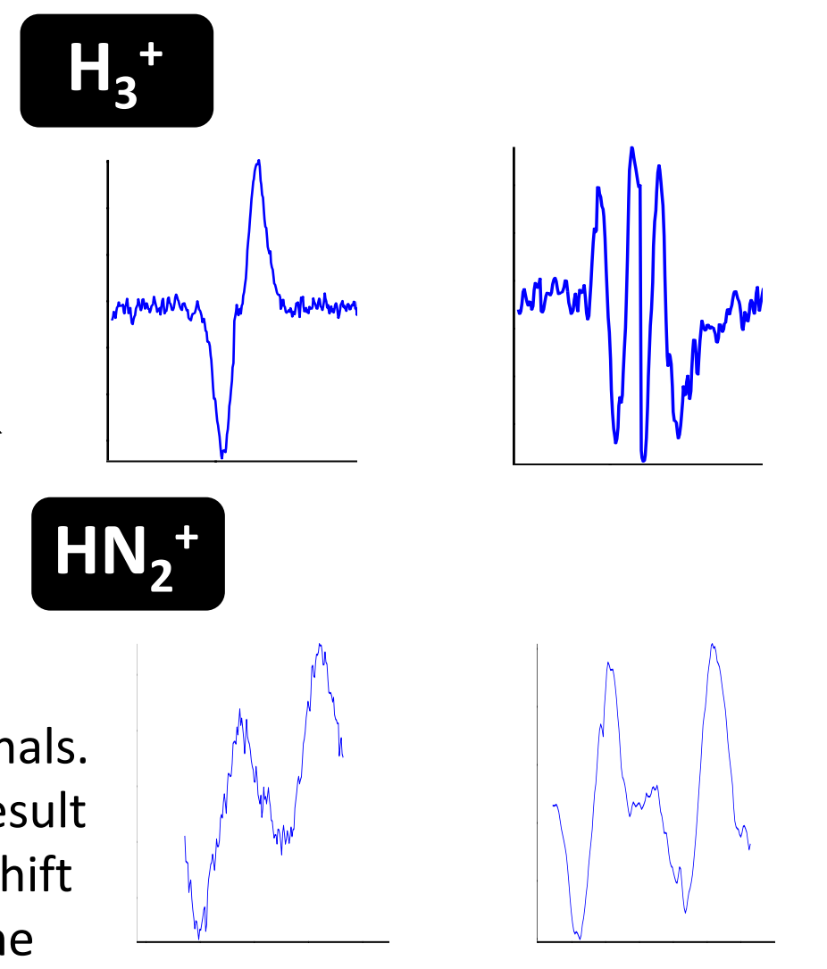


The slope of this Boltzmann plot corresponds to an $HN_2^+$ rotational temperature of ~35 K.

### Expected Lineshapes



### Observed Lineshapes



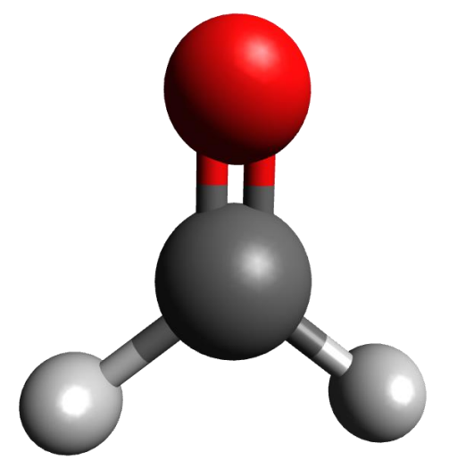
Expected and observed NICE-OHMS signals. The extra lobes are thought to be the result of narrowed linewidths and a Doppler shift inherent to the bidirectional cavity of the experimental set-up.

NICE-OHMS lineshapes from A. Foltynowicz, et al., International Symposium on Molecular Spectroscopy, The Ohio State University, Columbus, OH, 2009.

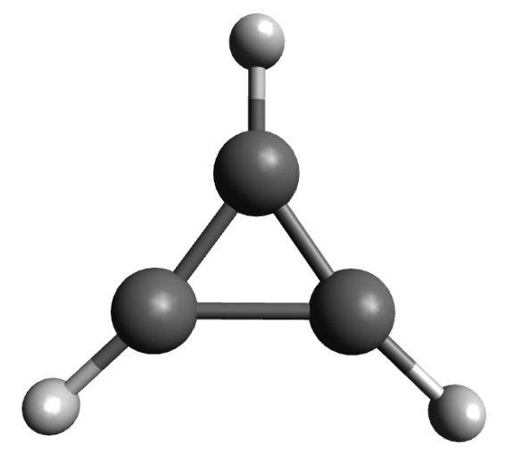
## Future Directions

With verification that the source is producing rotationally cold ions we move toward:

- A more thorough understanding of how modulating the discharge affects the observed NICE-OHMS lineshape
- The study of primary ions of astronomical significance
- A more powerful mid-IR light source
  - Optical-parametric oscillator
  - 2.5-3.9 µm
  - ~1.5 W Peak Power



$H_2CO^+$



$C_3H_3^+$

## Acknowledgments

We would like to thank Kyle N. Crabtree and Carrie A. Kaufman for optimizing the supersonic source design, Thomas Houlahan and Thomas Galvin for their help in designing the circuit used for discharge modulation, and Jessica Pearson for her work in putting the modulation circuit together.

Background image is from the Great Observatories Origins Deep Survey (GOODS) of the formation and evolution of galaxies and is accessible through the archives at http://hubblesite.org (January 5th, 2010).