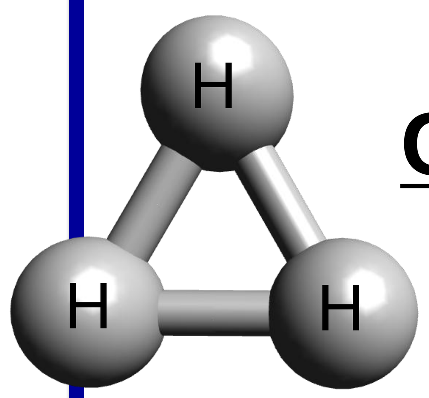
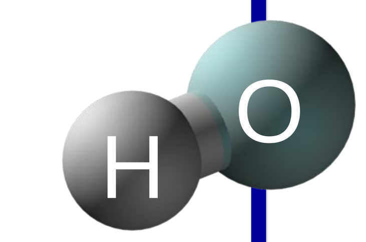
High precision and high accuracy spectroscopy of molecular ions



Charles R. Markus,* Adam J. Perry,* James N. Hodges,* G. Stephen Kocheril,* Benjamin J. McCall**

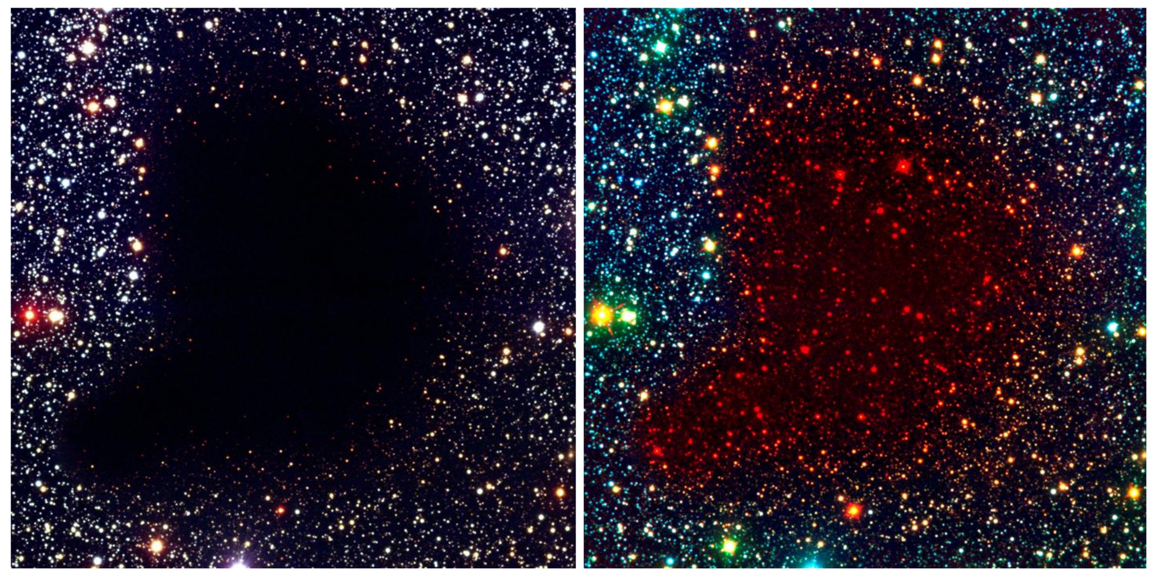
*Department of Chemistry, University of Illinois at Urbana-Champaign

**Departments of Chemistry, Astronomy, and Physics, University of Illinois at Urbana-Champaign



Why study molecular ions?

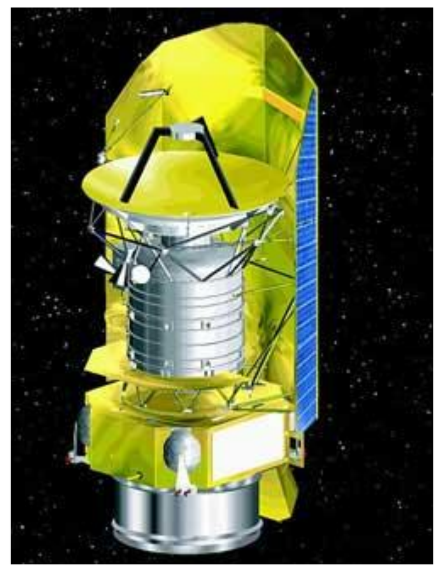
Astrochemistry



The Barnard 68 dark molecular cloud blocks starlight in the visible, but is transparent in the infrared. www.eso.org

The space between stars is far from empty. Over 150 species have been identified in the interstellar medium (ISM), and as methods improve this number bound to increase. Due to low number densities and low temperatures of the ISM only exothermic barrier-less reactions will take place. Ion-neutral interactions fulfill this requirement and dominate the dynamics. To be able to identify molecular ions in the often complex spectra measured by astronomers, high precision and accuracy spectra are needed from the laboratory. This in turn will allow for better characterization and understanding of dense molecular clouds and possibly the diffuse interstellar bands.

Molecular ions exist in cold environments, where emissions mainly result from rotational transitions in the THz/sub-mm. This region had long been out of reach due to water in the atmosphere, but has become available with the high altitude telescope SOFIA and the Herschel Space Observatory.



Sub-mm observatories SOFIA (left) and Herschel Space Observatory (right)

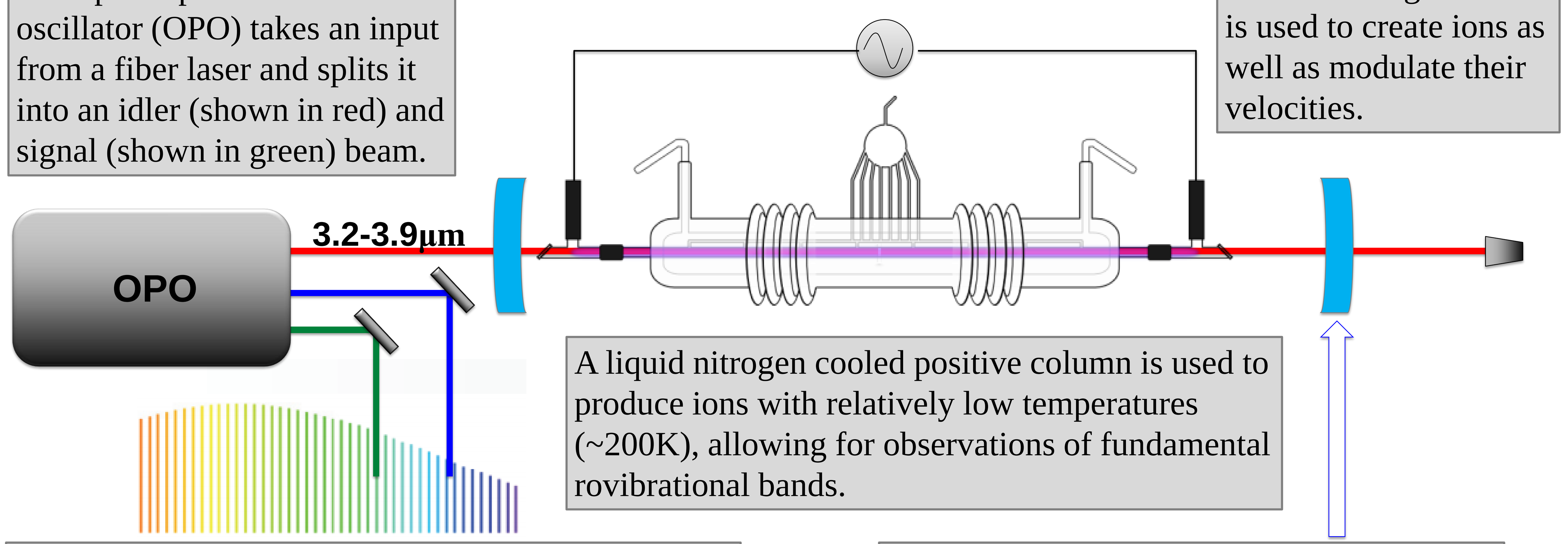
NICE-OHVMS

(**N**oise **I**mmune **C**avity **E**nhanced **O**ptical **H**eterodyne **V**elocity **M**odulation **S**pectroscopy)[3]

Instrument layout

The optical parametric oscillator (OPO) takes an input from a fiber laser and splits it into an idler (shown in red) and signal (shown in green) beam.

An alternating current is used to create ions as well as modulate their velocities.



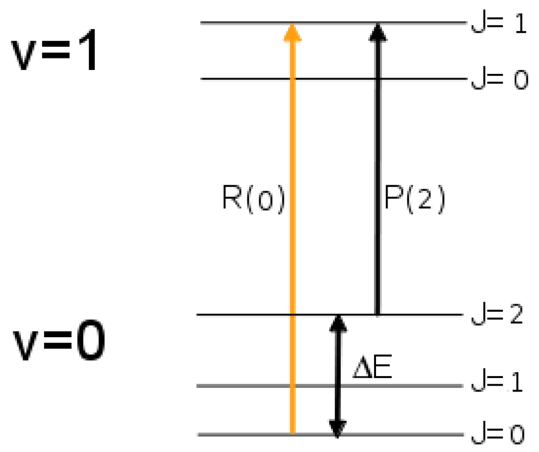
A liquid nitrogen cooled positive column is used to produce ions with relatively low temperatures (~200K), allowing for observations of fundamental rovibrational bands.

An optical frequency comb produces light at highly precise intervals. When mixed with the pump and signal beams, RF beat notes are generated allowing for precise calibration of the idler beam.

Spherical mirrors with 99% reflectivity produce an optical cavity around the sample, greatly increasing the effective path length.

Indirect Rotational Spectroscopy

Combination Differences



Depiction of how mid-IR transitions can be used to empirically determine rotational energy levels

Spectroscopy in the THz/sub-mm regime is challenged by the lack of quality sources and detectors. However, technology in the mid-IR does not have these hindrances. Depending on the molecule, rotational energy levels can be determined through combination differences or a full Hamiltonian fit of the rovibrational transitions.

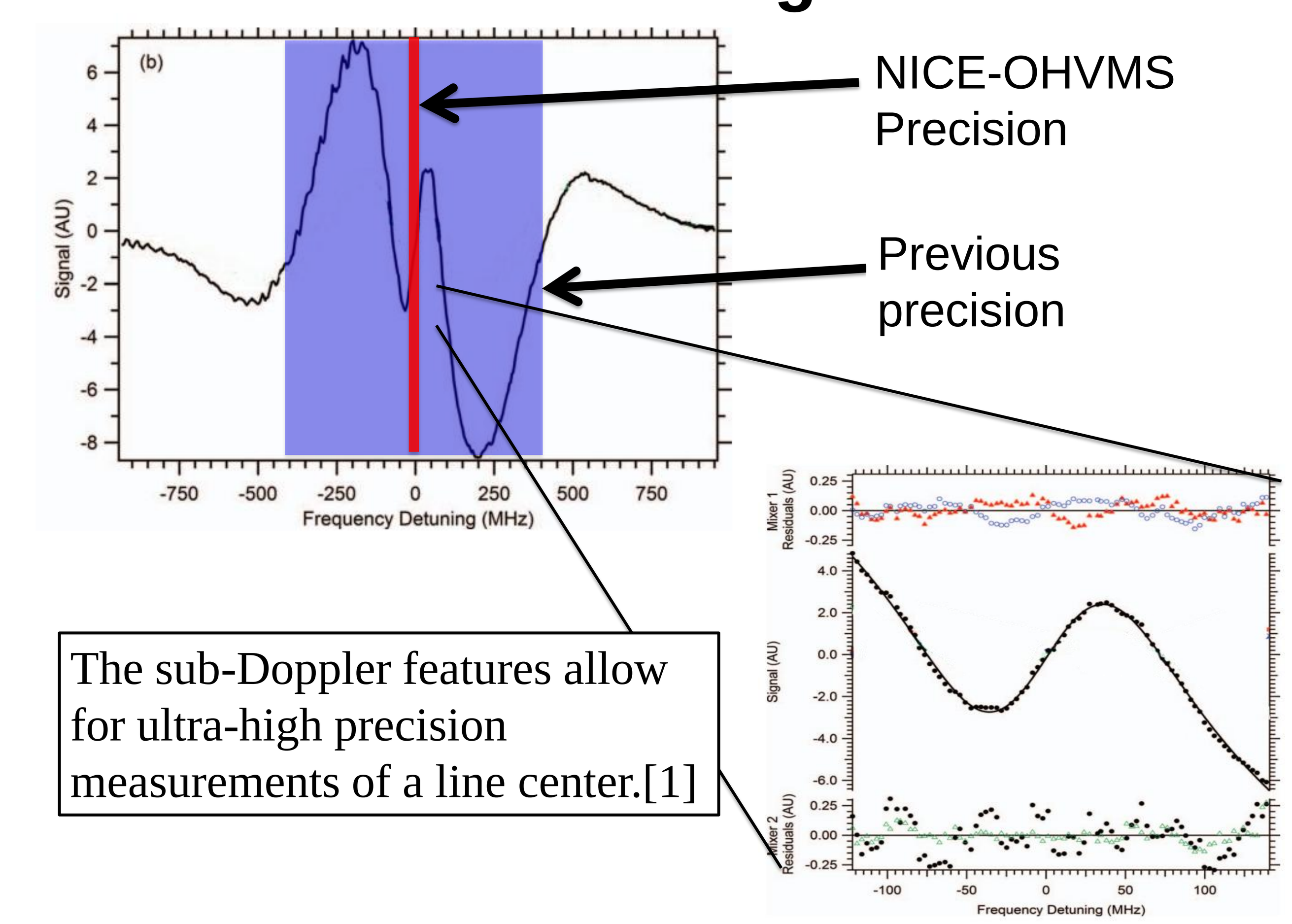
OH^+

Galaxy Arp 220 , a location where OH^+ has been used to determine the flux of cosmic rays. hubblesite.org

The molecular ion OH^+ has been observed in the ISM and is a key intermediate in the formation of water. Also, the ratios between OH^+ to H_3O^+ and H_2O^+ allows for the determination of cosmic ray ionization rates in diffuse molecular clouds.[4] This works seeks to improve known values of the pure rotational transitions.

Results and Future Work

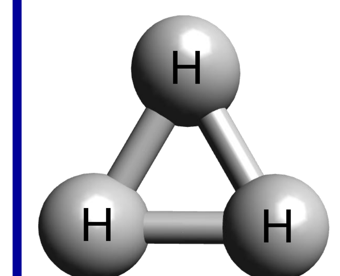
Improved uncertainty by orders of magnitude

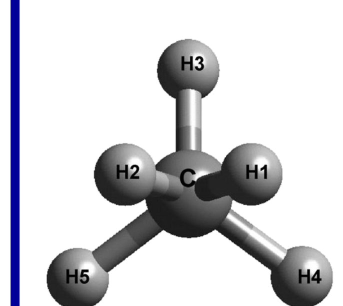


The sub-Doppler features allow for ultra-high precision measurements of a line center.[1]

Previously, the best uncertainties for molecular ions in the mid-IR has been roughly 100 MHz (0.01 cm^{-1}), and NICE-OHVMS is able to reach sub-MHz precision (10^{-3} cm^{-1}). Recently this has been used to measure seven transitions of HeH^+ to high precision and accuracy.[2] HeH^+ is the simplest heteronuclear molecule and these transitions aid in benchmarking state of the art *ab initio* theory. Preliminary results of OH^+ give confidence that similar improvements in precision over previous values is possible. This technique has also successfully investigated HCO^+, H_3^+, and CH_5^+.

Future Work





In the near future, a precise and accurate survey of OH^+ transitions in the mid-IR using NICE-OHVMS will be conducted. Combination difference analysis will enable indirect determination or pure rotational lines to aid astronomers. Along with this, surveys of the more complicated species H_3^+ and CH_5^+ will be pursued. Both are molecules important to the ISM, and learning more about their structure and chemistry could benefit both the astronomy and physics communities.[5]

References

[1] J.N. Hodges, A.J. Perry, P.A. Jenkins, II, B.M. Siller, and B.J. McCall,*J. Chem. Phys.* (2013), **139**, 164201.
[2] A.J.Perry, J.N. Hodges, C.R. Markus, G.S. Kocheril, and B.J. McCall , *J. Chem. Phys.* (2014) **141**, 101101.
[3] B. M. Siller, M.W. Porambo, A.A. Mills, and B.J. McCall*, Opt. Express* (2011), **19**, 24822-7.
[4] N. Indriolo, D.A. Neufeld, *et al., Astrophys. J.* (2015), **800**, 40.
[5] E.T. White, J. Tang, and T. Oka, *Science*,(1999) **284**, 135.