Continuous-wave cavity ringdown spectroscopy of molecular ions in a fast ion beam

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Motivation: To overcome the challenges previously faced during the spectroscopic study of molecular ions

Traditional plasma discharge sources produce ions at high temperatures, leading to a large partition function and resulting in spectral complexity and weak lines.

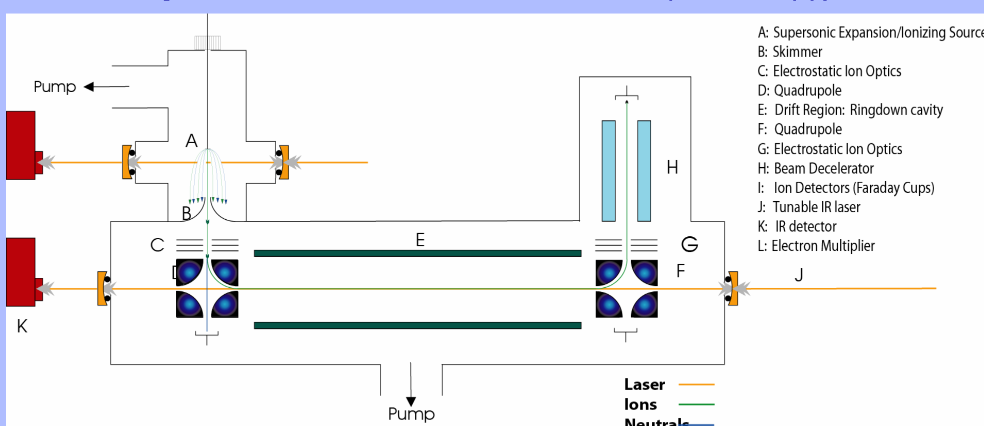
Supersonic expansions can be used to rotationally and vibrationally cool ions. High pressure gas (> 1 atm) is expanded through a pinhole or slit into a vacuum chamber at much lower pressure (< 10^{-3} atm). As the molecules expand they are adiabatically cooled.

Continuous-wave cavity ringdown spectroscopy (cw-CRDS) is a highly sensitive direct absorption technique. The output of a continuous-wave laser is coupled to a high finesse cavity formed from two high reflectivity mirrors. A piezo changes the length of the cavity, and the light couples to the cavity when in resonance. The light is diverted when resonance is achieved, and the intensity exponentially decays with a rate proportional to the cavity absorption. The minimum detectable absorbance is ~ 1×10^{-9} cm^{-1}.

The ionization efficiency in a plasma discharge source is typically ~10^{-6}, and so there are many neutrals present leading to spectral confusion.

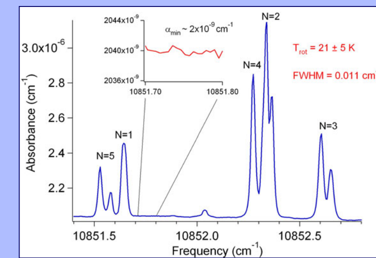
Fast Ion Beams (J.V. Coe, et al. 1989, J. Chem. Phys. 90, 3893) can be used to physically separate ions from neutrals. The ions are extracted from the source, accelerated, and focused using electrostatic ion optics. The resulting fast ion beam can then be turned 90º by an electrostatic quadrupole, allowed to drift through a field-free region, and then turned another 90º into a mass spectrometer. The beam in the drift region can be spectroscopically probed in a collinear configuration.

Design of SCRIBES
(Sensitive Cooled Resolved Ion BEam Spectroscopy)

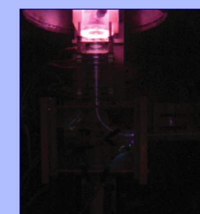


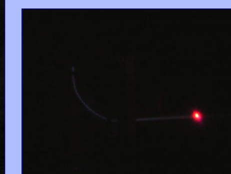
SCRIBES couples the sensitivity of cw-CRDS with a supersonic ion source and the ion beam technique to yield sensitive, cold, rotationally resolved spectra of molecular ions.

Progress on the SCRIBES experiment

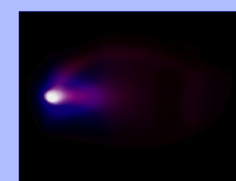


A cw-CRDS system has been built and tested with N_2^+ and a tunable external cavity diode laser at 925 nm. A supersonic discharge source was used for this experiment, and rotationally cold N_2^+ ions were observed.



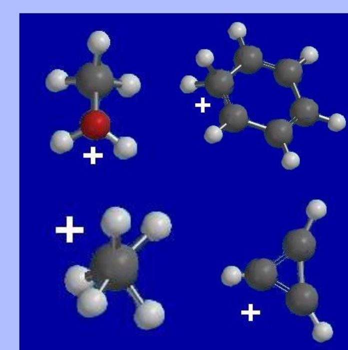


A 30 μA N_2^+ beam from an uncooled cathode dc discharge source has been achieved. This beam has been focused, collimated, and steered with ion optics. A cw-CRDS system at 925 nm has been coupled to the drift region and aligned with the ion beam. We are now in the process of searching for absorption lines from the 1-0 vibronic band of the N_2^+ $X\,^2\Sigma_g^+ \rightarrow A\,^2\Pi_u^-$ system.



A supersonic discharge source and skimmer are being designed while we install a differential pumping system with a 7500 cfm Roots pump and a 4780 cfm turbomolecular pump. We are also constructing a difference frequency generation laser system for cw-CRDS experiments in the 2 – 5 μm range.

The first targets for SCRIBES:



$CH_3OH_2^+$: important to gas phase interstellar chemistry; internal rotation & inversion

$C_6H_7^+$: precursor to interstellar C_6H_6; proton "walks" around ring

CH_5^+: precursor to interstellar CH_4, other hydrocarbons; highly fluxional molecule

$C_3H_3^+$: precursor to interstellar c-C_3H_2; simplest Hückel aromatic 4n+2

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