## LINESHAPE AND SENSITIVITY OF SPECTROSCOPIC SIGNALS OF $\mathrm{N}_2^+$ IN A POSITIVE COLUMN COLLECTED USING NOISE IMMUNE CAVITY ENHANCED OPTICAL HETERODYNE VELOCITY MODULATION SPECTROSCOPY

## ANDREW MILLS, BRIAN SILLER, <u>MICHAEL PORAMBO</u>, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; BENJAMIN J. McCALL, Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

Challenges to studying gas phase ions include the dilute analyte, Doppler line broadening, and a lack of ion/neutral discrimination. Techniques which provide high sensitivity, sub-Doppler features, and some form of ion/neutral discrimination increase the ability to study gas phase ions. Recently our group has used noise immune cavity enhanced optical heterodyne velocity modulated spectroscopy (NICE-OHVMS) to help overcome each of these challenges.

Using NICE-OHMS to probe a velocity modulated positive column produces a distinctive line shape. The high optical power from and geometry of the cavity saturates optical transitions and allows sub-Doppler Lamb dips to be observed. Depending on sideband frequency (1 or 9 times the free spectral range) the sub-Doppler features are closer together or further apart. The sub-Doppler features can then be used to measure the line-centers with high ( $\sim$ 1 MHz) precision and accuracy using an optical frequency comb.

The Kramers-Kronig relations describe how the absorption and dispersion are related to one another and can be used to obtain the absorption from the dispersion (and vice-versa). Owing to the phase dependent absorption signal produced with heterodyne spectroscopy, both absorption and dispersion signals can be obtained simultaneously. Two RF mixers (one for absorption and one for dispersion), each driving its own lock-in amplifier, are used to obtain a signal for ions and excited neutrals.

We will report a comparison of the sensitivities of several absorbance techniques to study a nitrogenic velocity modulated positive column including: direct absorption, cavity enhanced velocity modulation, heterodyne spectroscopy and NICE-OHMS, and show how the signal-to-noise ratio is increased by using NICE-OHMS.

Future plans for this technique include using a high power cw-OPO in the mid-IR to perform high precision vibrational spectroscopy of ions such as  $CH_5^+$ .