

PRECISION CAVITY ENHANCED VELOCITY MODULATION SPECTROSCOPY

ANDREW MILLS, BRIAN SILLER, *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*.

The study of gas phase ions has been recognized as an important field for many applications in combustion and physical chemistry, as well as astrochemistry. There are several challenges to overcome to study such molecular ions with high resolution spectroscopy, including ion/neutral discrimination, a dilute analyte, and Doppler line broadening. Recently our group has demonstrated the coupling of cavity enhanced absorption spectroscopy with velocity modulation (CEVMS) to help overcome these challenges. Cavity enhanced absorption spectroscopy can be more sensitive than non-cavity enhanced techniques, making it easier to study dilute analytes. Velocity modulation is used to distinguish between ions and neutrals.

The final challenge arises as the line frequency accuracy is often limited by the Doppler broadening of molecules due to the ensemble average of many molecules with different velocities. In CEVMS, because an optical cavity is used, the electric field intensity increases such that a Lamb dip is observed. Owing to the co-linear back-reflection, only molecules with zero velocity along the axis of laser propagation contribute to the Lamb dip. Thus, spectroscopy which records the transition frequencies of the Lamb dip have an inherently higher precision to the measurement. However, traditional wavemeters usually have accuracy specifications on the order of hundreds of MHz. Therefore, by using an optical frequency comb to measure the transition frequencies of the sub-Doppler Lamb dip, we can increase the accuracy and precision of infrared transitions that have (or have not yet) been measured.

In addition to demonstrating the use of Precision Cavity Enhanced Velocity Modulation Spectroscopy (P-CEVMS), we will discuss the power and pressure broadening of the Lamb dip. By studying the power dependence of the Lamb dip in N_2^+ , we hope to be able to obtain a measure of the transition strength for a single ro-vibrational line.