SUB-DOPPLER SPECTROSCOPY OF THE ν_2 FUNDAMENTAL BAND AND FIRST HOT BAND OF THE H_3^+ CATION

CHARLES R. MARKUS, PHILIP A. KOCHERIL, ANNE MARIE ESPOSITO, ALEX W SCHRADER, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; BENJAMIN J. McCALL, *Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL, USA*.

The simplest polyatomic molecule, H_3^+, serves as an important benchmark for *ab initio* theory and is an important constituent of the interstellar medium (ISM). In the ISM, H_3^+ initiates a chain of ion-neutral reactions which leads to more complex chemistry, and observations of H_3^+ can be used to measure interstellar conditions such as the cosmic ray ionization rate.[a] For *ab initio* theorists, accurate calculations of the rovibrational structure of H_3^+ require going beyond the Born-Oppenheimer approximation, and for its low-lying rovibrational states, agreement between theory and experiment has reached 0.001 cm^{-1}.[b] As these calculations begin to rival experimental measurements, new data are needed to benchmark future *ab initio* approaches.

Using the technique Noise-Immune Cavity-Enhanced Optical Heterodyne Velocity Modulation Spectroscopy (NICE-OHVMS)[c] to perform sub-Doppler spectroscopy and an optical frequency comb to accurately calibrate the frequency, we have expanded our survey of H_3^+ to include transitions from higher rotational levels in the fundamental band and transitions in the $2\nu_2^2 \leftarrow \nu_2^1$ hot band. Using combination differences, we have determined a number of energy level spacings in the ground state with an accuracy of ~ 5 MHz, which are directly compared with state of the art *ab initio* calculations. We also discuss our progress towards calculating "forbidden" rotational transitions, including a possible astrophysical maser,[d] which requires our newly measured hot band transitions.

[a] N. Indriolo, *Phil. Trans. R. Soc. A*, **370**, 5142 (2012).

[b] L. G. Diniz, J. R. Mohallem, A. Alijah, M. Pavanello, L. Adamowicz, O. L. Polyansky, and J. Tennyson, *Phys. Rev. A.*, **88**, 032506 (2013).

[c] J. N. Hodges, A. J. Perry, P. A. Jenkins II, B. M. Siller, and B. J. McCall, *J. Chem. Phys*, **139**, 164201 (2013).

[d] J. H. Black, *Phil. Trans. R. Soc. A*, **358**, 2515 (2000)