HIGH PRECISION SPECTROSCOPY OF CH_5^+ USING NICE-OHVMS

JAMES N. HODGES, ADAM J. PERRY, *Department of Chemistry, University of Illinois, Urbana, IL 61801*; BENJAMIN J. MCCALL, *Departments of Chemistry, Astronomy, and Physics, University of Illinois, Urbana, IL 61801*.

The elusive methonium ion, CH_5^+, is of great interest due to its highly fluxional nature. The only published high-resolution infrared spectrum remains completely unassigned to this date.[a] The primary challenge in understanding the CH_5^+ spectrum is that traditional spectroscopic approaches rely on a molecule having only small (or even large) amplitude motions about a well-defined reference geometry, and this is not the case with CH_5^+.

We are in the process of re-scanning Oka's spectrum, in the original Black Widow discharge cell, using the new technique of Noise Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy (NICE-OHVMS).[b,c] The high precision afforded by optical saturation in conjunction with a frequency comb allows transition line centers to be determined with sub-MHz accuracy and precision – a substantial improvement over the 90 MHz precision of Oka's work.

With a high-precision linelist in hand, we plan to search for four line combination differences to directly determine the spacings between rotational energy levels. Such a search is currently infeasible due to the large number of false positives resulting from the relatively low precision and high spectral density of Oka's spectrum. The resulting combination differences, in conjunction with state-of-the-art theoretical calculations from Tucker Carrington,[d] may provide the first insight into the rotational structure of this unique molecular system.

[a] E. T. White, J. Tang, T. Oka, *Science* (1999) **284**, 135–137.
[b] B. M. Siller, *et al. Opt. Express* (2011), **19**, 24822–24827.
[c] K. N. Crabtree, *et al. Chem. Phys. Lett.* (2012), **551**, 1–6.
[d] X. Wang, T. Carrington, *J. Chem. Phys.*, (2008), **129**, 234102.