SUB-DOPPLER SPECTROSCOPY OF THE $\nu_2$ FUNDAMENTAL BAND AND FIRST HOT BAND OF THE H$_3^+$ CATION

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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-OHVM$^c$) 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 $2\nu_2^+ \leftrightarrow \nu_2^+$ hot band. Using combination differences, we have determined a number of energy level spacings in the ground state with an accuracy of $\sim$ 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).