HIGHLY ACCURATE AND PRECISE INFRARED TRANSITION FREQUENCIES OF THE H_3^+ CATION

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Calculation of *ab initio* potential energy surfaces for molecules to high accuracy is only manageable for a handful of molecular systems. Among them is the simplest polyatomic molecule, the H_3^+ cation. In order to achieve a high degree of accuracy (<1 cm^{-1}) corrections must be made to the to the traditional Born-Oppenheimer approximation that take into account not only adiabatic and non-adiabatic couplings, but quantum electrodynamic corrections as well. For the lowest rovibrational levels the agreement between theory and experiment is approaching 0.001 cm^{-1}, whereas the agreement is on the order of 0.01 – 0.1 $\mathrm{cm}^{-1}$for higher levels which are closely rivaling the uncertainties on the experimental data[ab]. As method development for calculating these various corrections progresses it becomes necessary for the uncertainties on the experimental data to be improved in order to properly benchmark the calculations.

Previously we have measured 20 rovibrational transitions of H_3^+ with MHz-level precision, all of which have arisen from low lying rotational levels[cd]. Here we present new measurements of rovibrational transitions arising from higher rotational and vibrational levels. These transitions not only allow for probing higher energies on the potential energy surface, but through the use of combination differences, will ultimately lead to prediction of the "forbidden" rotational transitions with MHz-level accuracy.

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