

HIGHLY-ACCURATE EXPERIMENTALLY DETERMINED ENERGY LEVELS OF H_3^+

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H_3^+ is the simplest polyatomic molecule, and its rovibrational energy levels provide valuable benchmarks for *ab initio* theorists. Calculations of the H_3^+ potential energy surface which take into account effects beyond the Born-Oppenheimer approximation can predict rovibrational transitions from low lying states with an accuracy of 0.001 cm^{-1} ,^a and agreement is on the order of $0.01\text{--}0.1\text{ cm}^{-1}$ for transitions from higher levels. As the accuracy of theoretical methods begins to rival experimental uncertainties, new measurements are needed to benchmark future *ab initio* calculations.

In order to provide accurate experimentally determined energy levels, a survey of rovibrational transitions of H_3^+ has been collected using the sub-Doppler technique Noise-Immune Cavity-Enhanced Optical Heterodyne Velocity Modulation Spectroscopy (NICE-OHVMS).^b In total, we have measured 56 transitions in the $\nu_2 \leftarrow 0$ fundamental band,^{cd} 17 transitions in the $2\nu_2^2 \leftarrow \nu_2$ hot band, and 7 transitions in the $2\nu_2^2 \leftarrow 0$ overtone band with approximately 4 MHz uncertainty. For most transitions, this was an improvement by a factor of 40 or more. Combination differences were used to calculate ground state rotational levels relative to the lowest *ortho* and *para* states. A fit of the ground vibrational state to an effective Hamiltonian was used to determine energy levels relative to the forbidden (0,0) rotational state. Overall, 18 absolute energy levels were determined with uncertainties of approximately 0.0003 cm^{-1} (10 MHz). In addition, frequencies of forbidden rotational transitions were predicted, including a possible astrophysical maser.^e

^aL. G. Diniz, J. R. Mohallem, A. Alijah, M. Pavanello, L. Adamowicz, O. L. Polyansky, and J. Tennyson, *Phys. Rev. A*, **88**, 032406 (2013).

^bB. M. Siller, M. W. Porambo, A. A. Mills, and B. J. McCall, *Opt. Express*, **19**, 24822–7 (2011).

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

^dA. J. Perry, J. N. Hodges, C. R. Markus, G. S. Kocheril, and B. J. McCall, *J. Mol. Spectrosc.*, **317**, 71–73, (2015).

^eJ. H. Black, *Faraday Discussions*, **109**, 257–266 (1998).