THE VIBRATIONAL SPECTRUM OF FLOPPY PYRAMIDAL MOLECULES: NH_3 AND H_3O^+

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The vibrational spectra of ammonia and of the hydronium ion have been calculated from first principles. A new coordinate to describe the inversion together with conventional symmetry adapted internal valence coordinates have been used. The exact Kinetic Energy Operator has been obtained using Geometric Algebra. Several Taylor-like series expansions developed about two dimensional surfaces describing the most important symmetric configurations for both pyramidal molecules have been tested using the CCSD(T) *ab initio* method. Total electronic and nuclear energies have been extrapolated to the complete basis set limit, and first order relativistic corrections, together with Core-Valence correlation effects have been considered. Vibrational transitions have been accurately calculated till 15000 cm^{-1} using a variational approach. We obtained a mean absolute deviation of 1.73 cm^{-1} and of 2.18 cm^{-1} between the experimental and the calculated fundamentals of NH_3, and H_3O^+, respectively.