THE VIBRATIONAL SPECTRUM OF FLOPPY PYRAMIDAL MOLECULES: NH₃ AND H₃O⁺

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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 NH₃, and H₃O⁺, respectively.