A NUMERICAL-TENSORIAL "HYBRID" NUCLEAR-MOTION HAMILTONIAN AND DIPOLE MOMENT FOR SPECTRA CALCULATION OF POLYATOMIC NONRIGID MOLECULES

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The analysis and modelling of high-resolution spectra of nonrigid molecules require a specific Hamiltonian and group-theoretical formulation which differs significantly from that of more familiar rigid systems. Within the framework of the Hougen-Bunker-Johns (HBJ) theory[1], this work is devoted to the construction of a nonrigid Hamiltonian based on a suitable combination of numerical calculations for the nonrigid part in conjunction with the irreducible tensor operator method for the rigid part. A so-called "hybrid" model is thus introduced[2]. For the first time, a variational calculation from *ab initio* potential energy surfaces is performed using the hybrid formulation of the exact HBJ kinetic energy operator expressed in terms of vibrational, large-amplitude motion and rotational tensor operators through the use of both curvilinear and rectilinear coordinates. Group theory for nonrigid molecules plays a central role in the characterization of the overall tunnelling splittings and will be discussed. The construction of the dipole moment operator will be also examined.

Validation tests consisting in a careful convergence study of the energy levels as well as in a comparison of results obtained from independent computer codes are given for the nonrigid molecules CH_2, CH_3, NH_3 and H_2O_2. This work−combined with our recent method for constructing effective models[3]−will pave the way to the analysis of high-resolution spectra of larger nonrigid systems.

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