Abstract

In this talk, we will present an extension of our theoretical approach initially designed for semirigid molecules to more complex systems having at least one large amplitude motions (LAM) commonly known as nonrigid (floppy) molecules. This study will be essentially based on the Hamiltonian introduced in 1970 by Hougen, Bunker and Johns [1], the so-called HBJ model which could be considered as the nonrigid extension of the Watson-Eckart Hamiltonian. A complete and detailed derivation based on the HBJ approach with application to triatomic floppy molecules was made by Jensen [2]. A formulation in terms of internal coordinates has been carried out in [3]. One of the specificities of the present work is the possibility of using most of the tools previously developed in our laboratory for semirigid molecules (reduced Hamiltonian, compressed basis sets, tensor operators, etc.), with only some minor changes. Here, we have chosen a formulation quite different from what is usually done in the literature. To this end, the numerical treatment of the LAM coordinate is replaced by an algebraic formulation where all matrix elements (both for the small and large amplitude vibrations) are computed analytically to make variational calculations faster [4]. Illustrative examples will be given.