Highly correlated ab initio far infrared spectra of molecules with large amplitude torsional modes: dimethyl ether, methyl acetate and propane

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A theoretical study of the lowest frequency modes of several non-rigid molecules with two CH_3 tops has been carried out. The main aim of these works was to give a support to their spectral analyses [1,2,3] in the far infrared region. This was carried out, on one hand, to provide some estimates of the Hamiltonian parameters based on ab initio calculations that could find out the unphysical parameters in a normally fitted effective Hamiltonian. On the other hand, to predict either some faint bands and forbidden ones or the splittings coming from the large amplitude torsional modes.

With this purpose, a variational model in three dimensions [4] was proposed to compute the excited energy levels of the two torsional modes and the lowest frequency bending mode of molecules as dimethyl ether [5,6,7], methyl acetate [8] and propane [9]. The potential energy surfaces are computed using CCSD(T) ab initio calculations and they are vibrationally corrected. In spite of the quality of these highly correlated potentials in molecules with similar structures, it was proven that an empirical adjustment of the surfaces would enclose accurately the experimental and theoretical frequency residuals.

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