AB INITIO AND MODEL-HAMILTONIAN STUDY OF THE TORSIONAL VARIATION OF THE THREE CH STRETCHING NORMAL MODES IN METHANOL

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The ν_2, ν_3 and ν_9 CH stretching modes of methanol in the 3μm region exhibit a significant amount of torsion-vibration interaction, as illustrated for ν_9 by the facts that: (i) the three hydrogen atoms each pass through a plane of symmetry of the molecule twice during the course of one full internal rotation motion, once at a minimum and once at a maximum in the three-fold potential energy curve, (ii) the H atom in the plane of symmetry is nearly motionless for the ν_9 mode, and therefore (iii) the property of remaining motionless must be transferred from one H to another six times during one full internal rotation motion. In this talk we examine quantitatively the general phenomenon of torsion-vibration interaction in the methyl top stretching modes in two ways. First, we present plots of normal modes produced in Gaussian projected frequency calculations that are expressed either in terms of several sets of internal coordinates, or in terms of Cartesian displacement vectors for the methyl hydrogen atoms. Some of these plots display a nearly three-fold sine or cosine behavior, where the sine or cosine behavior is dictated by group-theoretical symmetry arguments. Other plots display stunning features ranging from loss of simple three-fold oscillatory pattern to cusp-like peaks or dips. Somewhat surprisingly, none of our ab initio plots for methanol exhibit a sign change after a 2π internal rotation of the methyl top. Second, we present a relatively simple model for the three CH stretching motions, characterized by three parameters associated with: (i) a vibrational A/E energy difference, (ii) a Jahn-Teller-like torsion-vibration interaction term within the vibrational E state, and (iii) a Renner-Teller-like torsion-vibration interaction term within the E state. This model gives nearly quantitative agreement with both the regular and irregular features of the ab initio plots. The good agreement suggests that various aspects of the physics of the model can be used to understand the quite complicated Gaussian normal mode results for ν_2, ν_3 and ν_9.