Ab Initio and Model-Hamiltonian Study of the Torsional Variation of the CH Stretching Normal Modes in Methanol

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The fundamental ν_3 (A′), ν_2 (A′) and ν_9 (A″) CH stretching modes of methanol, centred around 2844, 2970, and 2999 cm^{-1} [1] respectively, in the 3μm region exhibit a significant amount of torsion-vibration interaction, as illustrated for the ν_9 mode 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, based on work about to be submitted to the J. Mol. Spectrosc. [2], 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 a loss of the 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 2x2 model for the three CH stretching motions, which considers ν_2 and ν_9, but excludes ν_3. The model is characterized by three parameters associated with: (i) an average vibrational frequency characterizing ν_2 and ν_9, when they are considered to be different components of the same vibrational E state, (ii) a Jahn-Teller-like torsion-vibration interaction term within this vibrational E state, and (iii) a Renner-Teller-like torsion-vibration interaction term within this E state. Such a model gives nearly quantitative agreement with both the regular and irregular features of the ν_2 and ν_9 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 and ν_9.

Finally, a highly simplified example calculation will be given to illustrate the changes that will be necessary to move from the usual diabatic torsion-vibration treatments in the literature to an adiabatic treatment that uses Gaussian projected frequency output directly in the calculation.

[1] Serrallach, A., Meyer, R. And Gunthard, H.H. J. Mol. Spectrosc. (**1975**) *52*, 94-120.
[2] Li-Hong Xu, Jon T. Hougen, and R. M. Lees, J. Mol. Spectrosc. (**2013**) to be submitted.