TORSION-VIBRATION, TORSION-ROTATION, AND VIBRATION-ROTATION INTERACTION CONSTANTS FOR CH_3OH FROM AB INITIO CALCULATIONS

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This is a progress report on our effort to investigate the possibility of obtaining useful spectrosopic information from ab initio calculations. Previously, we have shown[a] that quantum chemistry results for methanol at the top and bottom of the torsional barrier could be used to determine the cos3γ dependence of the torsional potential energy (i.e., the barrier height) to better than 0.5 %, and the cos3γ dependence of the rotational constants (three diagonal and one off-diagonal) to accuracies ranging from 7 % to 40 %. Results for acetaldehyde were about ten times worse, though these large discrepancies could be improved significantly by an empirical adjustment procedure. We then have shown[b] that G98 delivered very smooth force constant plots as a function of angle along the internal rotation coordinate (defined to be 0° at the bottom and 60° at the top of the barrier), and that when symmetrized coordinates (in the permutation inversion group G_6) were used, these plots exhibited the sin3γ or cos3γ behavior expected from the symmetry species of the pair of vibrational coordinates multiplied by the force constant.

In the present paper we investigate algebraically the meaning of various off-diagonal elements occurring in a Hessian matrix obtained by rotating the Cartesian Hessian matrix (containing second derivatives of the potential surface) to a coordinate system consisting of 3N-7 small-amplitude vibrations (where N is the number of atoms in the molecule), one large-amplitude vibration (the torsion), three overall rotations of the molecule, and three translations of the molecule. We then compute these elements numerically using quantum chemistry methods. Finally we discuss how these elements can be applied to analyses of vibration-torsion-rotation bands of methanol.

[a] L.-H. Xu, R.M. Lees, and J.T. Hougen, J. Chem. Phys. 110, 3835-3841 (1999).

[b] L.-H. Xu, J.T. Hougen, R.M. Lees, and M.A. Mekhtiev, J. Mol. Spectrosc. 214, 175-187 (2002).