THEORETICAL STUDIES OF THE VIBRATIONAL SPECTROSCOPY AND A/E TUNNELING SPLITTINGS OF METHANOL AND ITS DEUTERATED ANALOGUES

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The molecular eigenstates of methanol and its deuterated analogues are calculated using a combination of Van Vleck perturbation theory and variational calculations following the approach of Castillo and Sibert[a]. The energies, including torsional tunneling splittings, are compared with available spectroscopic data for all the fundamentals. Excellent agreement is found. Varying the torsional mass, correlation plots are constructed in order to elucidate the complex role of torsion-vibration coupling. The starting point for these calculations is a potential energy force field calculated at the CCSD(T) level using the cc-pVTZ basis set. This force field describes the coupled molecular vibrations, including the cubic and quartic anharmonicites, as a function of the torsional coordinate.

[a]E.L. Sibert and J. Castillo-Chará, J. Chem. Phys. **119**, 11671 (2003).