AB INITIO CALCULATIONS OF VIBRATIONAL MODE COUPLING IN METHANOL

DAVID S. PERRY and J. GO, *Department of Chemistry, University of Akron, Akron, OH 44325-3601*.

Methanol is important in combustion both as a fuel and as an intermediate. Vibrational mode coupling results in energy flow within vibrationally excited methanol and thereby affects its subsequent reactivity. The large amplitude torsional mode of methanol is at the center of the present study and may serve as a model for the behavior of other combustion intermediates with large amplitude vibrations.

Coupling between the methyl C-H stretches and the torsion in methanol results in a 42 cm^{-1} splitting between the ν_2 and ν_9 modes and results in an inversion of the torsional tunnelling splitting in these modes. Ab initio calculations (up to MP2/6-311G+(3df,2p) and MP4/6-311G+(2d,p)) appear to converge to a ν_2-ν_9 splitting of 60 cm^{-1}, still substantially larger than the experimental value. This difference is attributed to 1:2 stretch-bend resonances involving the methyl C-H bonds.

The torsional tunnelling splitting in methanol decreases monotonically from 9.1 cm^{-1} in the ground state to 1.6 cm^{-1} at the fifth overtone of the O-H stretch. This trend indicates an increase in the torsional barrier height with vibrational excitation of the O-H bond. Optimized ab initio calculations indicate that the torsional barrier increases as the O-H bond length is either lengthened or shortened from the equilibrium distance.