VIBRATIONAL DEPENDENCE OF THE TORSIONAL BARRIER HEIGHT AND THE A/B INTENSITY EVOLUTION IN THE OH OVERTONE SPECTRA OF METHANOL

M. ABBOUTI TEMSAMANI, LI-HONG XU, *Department of Physical Sciences, University of New Brunswick, N.B. Canada E2L 4L5*; D. S. PERRY, *Department of Chemistry, University of Akron, Ohio 44325-3610.*

Rizzo and co-workers[a] have used supersonic-jet infrared-laser-assisted photofragment spectroscopy (IRLAPS) to record the O-H stretching overtone spectra of CH_3OH. Their analysis of the rotation-torsion structures revealed the following interesting features: (i) the torsional A-E splitting decreases monotonically as ν_{OH} increases, indicating increase of the torsional barrier height V_3, (ii) *a*-type transitions become dominant at higher excitations of the OH stretching vibration, (iii) a 1:1 anharmonic resonance occurs between the OH stretch and CH stretch vibrations, reaching its maximum in the $5\nu_1$ region.

The third observation has been recently studied by Quack and Willeke[b] for the case of CD_2HOH, by means of *ab initio* five-dimensional potential energy and dipole moment surfaces. The present contribution explores possible *ab initio* explanations for the first two observations. At the MP2 level with 6-311G+(3df,2p) basis set, effective one-dimensional functions for the potential energy, dipole moment (*a* and *b* directions), barrier height and torsional constant F have been obtained by scanning the O-H bond length in order to take into account the mechanical and electrical anharmonicities. All *ab initio* quantities have been expressed as Taylor expansions in the dimensionless coordinate, q. Calculations have been carried out in the harmonic basis set to yield vibrational energies and eigenfunctions. The latter have been used to compute the patterns of the barrier height V_3, the torsional constant F, and the evolution of the infrared intensity ratio I_a/I_b, as functions of the OH vibrational quantum number. All our *ab initio* results agree with the experimental observations in points (i) and (ii) above. Details of the calculations, the corresponding results and the comparison to experimental data will be presented.

[a]O. V. Boyarkin, T. R. Rizzo and David S. Perry, *J. Chem. Phys.* **110**, 11359 (1999).
[b]M. Quack and M. Willeke, *J. Chem. Phys.* **110**, 11958 (1999).