A TEST OF THE ADIABATIC SEPARATION OF THE TORSION AND CH-STRETCH VIBRATIONS IN METHANOL

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High resolution spectroscopy has revealed inverted torsional tunneling splittings for the methanol asymmetric CH stretch vibrations (ν_2=1 and ν_9=1) and for some other methanol fundamentals. The lowest order torsion-vibration coupling, incorporated in a 4-dimensional model Hamiltonian[a] was sufficient to account for the torsional structure of the CH fundamentals. Fehrensen *et al.b*[b] have used an adiabatic separation of the torsion from the other 11 vibrations, together with *ab initio* calculations and the concept of geometric phase to successfully reproduce the ordering of the observed torsional levels in methanol. The approximate adiabatic separation of variables is an essential tool used throughout chemistry and spectroscopy to make difficult problems tractable. The most famous example is the Born-Oppenheimer separation of the nuclear and electronic degrees of freedom. This torsion-vibration problem provides the opportunity to test the adiabatic approximation against an exact calculation. In this work, we compare the exact solution of the 4-dimensional CH-stretch-torsion Hamiltonian with an approximate adiabatic solution of the same Hamiltonian. We find that the adiabatic approximation gives the correct ordering of the lowest torsional levels, but that the torsional splittings are not quantitatively accurate. For high torsional states ($\nu_{12} \geq 2$), the exact model calculation gives vibrations are approximately two-fold and four-fold degenerate. This indicates that the ν_2 and ν_9 vibrations approach degeneracy at high torsional excitation and that torsional and vibrational degrees of freedom effectively decouple. This behavior was not modeled correctly in the adiabatic approximation. Non-adiabatic effects are evident as off-diagonal coupling matrix elements in the adiabatic basis. We report the scaling properties of these IVR coupling matrix elements in this torsion-vibration problem.

[a] X. Wang, D. S. Perry *J. Chem. Phys.* **109**,10795 (1998)

[b] B. Fehrensen, D. Luckhaus, M. Quack, M. Wileke, and T. R. Rizzo *J. Chem. Phys.* **119**, 5534 (2003)