CH STRETCH VIBRATIONAL SPECTROSCOPY AND TUNNELING DYNAMICS IN VINYL RADICAL

FENG DONG, M. A. ROBERTS, R. S. WALTERS, and D. J. NESBITT, *JILA, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO. 80309*.

Vinyl radical is a crucially important species in combustion models, which exhibits large amplitude tunneling of the lone CH moiety over an in-plane barrier. High resolution jet cooled near IR spectra of the methylenic CH_2 stretch have been obtained in a slit supersonic expansion, revealing rotationally resolved bands with a even/odd Ka intensity signature inconsistent with 3:1 H atom exchange nuclear spin statistics for transitions out of a single tunneling state. However, this would be consistent with expectations if the transitions from upper and lower tunneling states are overlapped within our resolution limit. To explore this possibility, we have developed a high level zero point corrected tunneling potential surface from CCSD(T) ab initio calculations (AVnZ, n=2,3,4) and extrapolating to the complete basis set limit. This permits tunneling splittings to be calculated for both ground and vibrationally excited states, and to make direct comparison with both our current near IR as well as previous mid IR and microwave experimental results.