

## FULL-DIMENSIONALITY QUANTUM CALCULATIONS OF ACETYLENE/VINYLDENE ISOMERIZATION

ALEX BROWN, J. M. BOWMAN, S. ZOU, *Department of Chemistry and Cherry L. Emerson Center for Scientific Computation, Emory University, Atlanta, GA 30322.*

The isomerization of acetylene to vinylidene is examined theoretically in full-dimensionality (six degrees-of-freedom) using a new ab initio potential energy surface <sup>a</sup>. Eigenfunctions and eigenvalues of the exact Hamiltonian, for zero total angular momentum, are obtained using a series of novel truncation/recoupling procedures that permits calculations up to very high energies. The Hamiltonian is given in diatom-diatom Jacobi coordinates, with the choice H<sub>2</sub>-C<sub>2</sub> for the two diatoms to exploit the full permutational symmetry of the problem. By examining expectation values of the eigenfunctions, a number of states are clearly identified with vinylidene-like characteristics. Corresponding calculations are also done for C<sub>2</sub>D<sub>2</sub>. Full dimensional simulations of the photodetachment spectra of [C<sub>2</sub>H<sub>2</sub>]<sup>-</sup> and [C<sub>2</sub>D<sub>2</sub>]<sup>-</sup> are done (within the Franck-Condon approximation) and compared to the experimental ones.

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<sup>a</sup>S. Zou and J. M. Bowman, Chem. Phys. Lett. 368, 421 (2003).