FULL-DIMENSIONALITY QUANTUM CALCULATIONS OF ACETYLENE/VINYLIDENE ISOMERIZATION

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The isomerization of acetylene to vinylidene is examined theoretically in full-dimensionality (six degrees-of-freedom) using a new ab initio potential energy surface [a]. 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_2-C_2 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_2D_2. Full dimensional simulations of the photodetachment spectra of $[C_2H_2]^-$ and $[C_2D_2]^-$ are done (within the Franck-Condon approximation) and compared to the experimental ones.

[a] S. Zou and J. M. Bowman, Chem. Phys. Lett. 368, 421 (2003).