FULL-DIMENSIONALITY QUANTUM CALCULATIONS OF ACETYLENE/VINYLDENE 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.