

## THEORETICAL STUDY OF THE SPECTROSCOPY AND DYNAMICS OF THE VINYLIDENE-ACETYLENE ISOMERIZATION

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The results of a 5D ab initio quantum dynamical study of the vinylidene - acetylene isomerization reaction are presented. The study is based on a new ab initio potential energy surface for the planar system, obtained with the CCSD(T) method and the cc-pVTZ basis set. The dynamics is studied with grid methods, using 4-atom Jacobi-like coordinates and wave packet propagation techniques. The results of a 3D treatment, including the 2 angular degrees of freedom and the C-C stretching mode, have been reported earlier in the literature<sup>a</sup>. Including all (planar) degrees of freedom, the experimental photodetachment spectrum of Lineberger and coworkers<sup>b</sup> is very well reproduced. Furthermore, lifetimes for broadband excitation and for individual vibrational levels of vinylidene have been computed, the latter with the aid of filter diagonalization techniques. The lifetimes are 2-3 orders of magnitude longer than previously believed, indicating a surprising stability of this reactive intermediate. Similar results have been obtained for the deuterated species, D<sub>2</sub>CC supporting the above conclusions.

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<sup>a</sup>R. Schork, and H. Köppel, *Theor. Chem. Acc.* 100, 204 (1998).

<sup>b</sup>K. M. Ervin, J. Ho, and W. C. Lineberger, *J. Chem. Phys.* 91, 5974 (1989).