ELECTRONIC EFFECTS OF LARGE AMPLITUDE MOTION: DIPOLE MOMENTS OF VIBRATIONALLY EXCITED S_0 ACETYLENE

BRYAN M. WONG, ADAM H. STEEVES, AND ROBERT W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*.

Large amplitude vibrational motions often result in changes in electronic structure. In fact, electronic properties can be used to identify eigenstates in which vibrational excitation is localized in a single local stretching or bending motion. The vinylidene-acetylene isomerization and the local CH stretch of acetylene are investigated using a reaction path-like formalism. The one dimensional reaction path potential makes use of an internal coordinate path Hamiltonian which gives a well-defined path with no numerical complexity. Eigenfunctions and eigenvalues of this one-dimensional Hamiltonian are obtained for both the local CCH bend and CH stretch up to very high energies. By examining expectation values of dipole moments, the possibility of using Stark spectroscopy for identifying highly excited local-mode-limit vibrational states is proposed. Comparisons to available experimental and theoretical models are also reported.