AB INITIO CALCULATION OF JAHN-TELLER COUPLING CONSTANTS

BRIAN E. APPLEGATE, TERRY A. MILLER, The Ohio State University, Dept. of Chemistry, Laser Spectroscopy Facility, 120 W. 18th Avenue, Columbus, Ohio 43210; and TIMOTHY A. BARCKHOLTZ, JILA, National Institute of Standards and Technology and The Department of Chemistry and Biochemistry, University of Colorado Boulder, CO 80309 - 0440.

A recently developed ab initio method for calculating Jahn-Teller constants has been employed to investigate the Jahn-Teller effect in the methoxy family of radicals (CH₂O, CF₃O, CH₃S, and CF₃S) as well as the cyclopentadienyl radical (C₅H₅). This method combines the complete active space self-consistent field (CASSCF) wavefunction available in the Gaussian94/98 program and the generalized restricted Hartree-Fock (GRHF) wavefunction available in the CADPAC program. The energy of the symmetric configuration of the nuclei is calculated, using a CASSCF wavefunction, as a conical intersection between the two components of the degenerate electronic state, whose degeneracy is lifted by the Jahn-Teller effect. The energy of the distorted configuration is calculated with a CASSCF wavefunction that has the same occupancies and active space as the conical intersection calculation. The difference in the energy of these two calculations corresponds to the linear Jahn-Teller stabilization energy. In addition to determining the energy of the symmetric configuration, the conical intersection calculation also determines the vector along which the molecule will distort. By projecting this vector onto the normal modes of the molecule, obtained from a GRHF calculation, the experimentally observable linear Jahn-Teller coupling constants are estimated. Details of the computational approach along with results on systems presently investigated will be presented.