AB INITIO CALCULATION OF JAHN-TELLER COUPLING CONSTANTS

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We have developed a general method for the calculation of Jahn-Teller coupling constants by ab initio methods. The vibrational frequencies are calculated using a generalized restricted open-shell Hartree-Fock (GROHF) wavefunction using the ab initio program CADPAC. The energy of the symmetric configuration, which is a cusp, is calculated as a conical intersection using a complete active space self-consistent field (CASSCF) wavefunction, available in Gaussian94. The energy of the distorted configuration is calculated using the same CASSCF active space and occupations. The difference in energy of these two calculations is the Jahn-Teller stabilization energy. In addition to the total energy of the radical at the cusp, the conical intersection wavefunction calculates the vector along which the molecule will distort. This vector is projected onto the normal modes of the molecule, obtained via the GROHF calculation, which allows estimates of the experimentally observable linear Jahn-Teller coupling constants to be obtained. This approach has been applied to the methoxy radicals (CH_3O, CF_3O, CH_3S, and CF_3S) and several substituted benzene cations, 1,3,5-$C_6X_3Y_3$ (X = H, F; Y = H, F, Cl). The computational approach will be presented in detail and comparisons between the calculated coupling constants and those deduced from experimental spectra will be made.