AB INITIO CALCULATION OF THE SPECTROSCOPICALLY OBSERVABLE JAHN-TELLER CONSTANTS OF THE $\widetilde{X}^2\mathrm{E}_1''$ STATE IN THE CYCLOPENTADIENYL RADICAL

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Recently developed methods[a] for calculating Jahn-Teller coupling constants using commercially available *ab initio* programs have made it possible to attack some long standing problems in understanding molecules exhibiting Jahn-Teller effects in multiple vibrational modes. One of these problems has been the analysis of the vibronic structure in the $\widetilde{X}^2\mathrm{E}_1''$ state of the cyclopentadienyl radical, $\mathrm{C_5H_5}$. This radical nominally possesses D_{5h} symmetry; however, upon distortion the symmetry is reduced to C_{2v}. In accordance with this a CASSCF/6-31G* calculation with the 5 π electrons in the 5 π orbitals as the active space finds the compressed dienylic geometry as the global minimum on the potential energy surface, while only an insignificant 4 cm^{-1} barrier is predicted for internal rotation to the elongated allylic geometry. A conical intersection calculation on the electronic states that correspond to these two geometries indeed recovers the symmetric D_{5h} geometry. Using these calculations, as well as a generalized restricted Hartree-Fock calculation to generate normal modes and frequencies we are able to describe the nature of this distortion in terms of four normal modes of vibration. Only the three modes lowest in energy make significant contributions to the distortion and as such have significant linear Jahn-Teller coupling constants. The calculated value of the Jahn-Teller coupling constants and unperturbed vibrational frequencies are extremely useful for the analysis of the laser excited, dispersed fluorescence spectra of the cyclopentadienyl radical.

[a]Barckholtz T. A.; Miller T. A., *J. Phys. Chem.*, **1999**, *103*, 2321.