HIGH-RESOLUTION PFI-ZEKE PHOTOELECTRON SPECTROSCOPY OF THE CYCLOPENTADIENYL RADICAL

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This presentation summarizes the results of the first photoelectron spectroscopic study of the cyclopentadienyl radical. The cyclopentadienyl radical was produced in a supersonic expansion by photolysis of cyclopentadiene at 248 nm using the method described in Ref. a. PFI-ZEKE photoelectron spectra were recorded using two different excitation schemes. In the first experiment single-photon excitation from the $\tilde{X}\ ^2\mathrm{E}_1''$ ground state of the radical was used to study the ground state of the cyclopentadienyl cation. In the second experiment, a resonance-enhanced two-photon excitation scheme via the vibrationless transition to the $\tilde{A}\ ^2\mathrm{A}_2''$ studied in Ref. b provided access to the first electronically excited state of the cyclopentadienyl cation. The analysis of the spectra reveals that the ground state of the cyclopentadienyl cation is a triplet state of electronic symmetry $^3\mathrm{A}_2'$ and the first excited state is a singlet of symmetry $^1\mathrm{E}_2'$, which is subject to a pronounced Jahn-Teller distortion. The results of *ab initio* calculations together with a preliminary analysis of the Jahn-Teller effect in the $^1\mathrm{E}_2'$ state are presented.

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a. S. Willitsch, J.M. Dyke and F. Merkt, Helv. Chim. Acta, **86**, 1152 (2003).
b. L. Yu, S.C. Foster, J.M. Williamson, M.C. Heaven and T.A. Miller, J. Chem. Phys. **92**, 4263 (1988).