PHOTOELECTRON SPECTROSCOPY OF CYCLOPENTADIENIDE: ANALYSIS OF THE JAHN-TELLER EFFECTS IN THE CYCLOPENTADIENYL RADICAL

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The 351.1 nm photoelectron spectrum of cyclopentadienide anion has been measured. The spectrum, which reveals that the electron affinity of the cyclopentadienyl radical is 1.812 $\pm$ 0.005 eV, exhibits rich vibronic structure in the $\tilde{X}^2E_1''$ state. The degenerate states interact via linear Jahn-Teller couplings along the e_2' modes. Equation-of-motion coupled-cluster calculations (EOMIP-CCSD) have been performed, and the coupling coefficients have been derived. Only negligible displacements from the anion to radical ground states are predicted along the a_1' mode (ring stretching), suggesting that the spectrum consists primarily of activity involving the Jahn-Teller modes. Model diabatic potentials of the degenerate states have been constructed around the anion geometry in terms of the anion reduced normal coordinates. In addition to the linear Jahn-Teller couplings, bilinear couplings between the a_1' and e_2' modes have also been included in the model potentials. Simulation based on the model Hamiltonian reproduces the observed spectrum very well, identifying the vibronic levels of the radical. The bilinear couplings have significant effects on the simulation, analogous to the situation for another Jahn-Teller system, methoxy radical. Our results are compared with a previous dispersed fluorescence study by Miller and coworkers. Supported by NSF and AFOSR.