FULL ANALYSIS OF THREE-STATE-VIBRONIC COUPLING IN THE PYRAZOLYL-d_3 RADICAL

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The 351.1 nm photoelectron spectrum of pyrazolide-d_3 anion has been measured. The photoelectron angular distributions indicate the presence of nearly-degenerate electronic states of the pyrazolyl-d_3 radical. Equation-of-motion coupled-cluster calculations (EOMIP-CCSD) have been performed to study low-lying states of the radical. The calculations lead us to conclude that three electronic states, energetically close to each other, are accessed in the photodetachment process. Strong interactions of the pseudo-Jahn-Teller type within each pair of the three states are evident in the calculations for the radical at the anion geometry. Model diabatic potentials of the three states have been constructed around the anion geometry in terms of the anion reduced normal coordinates up to second-order. Parameters of the model potentials have been derived from the EOMIP-CCSD. Simulation of the spectrum based on the model Hamiltonian has been performed, treating all the vibronic interactions among the three states simultaneously. The simulation reproduces the fine structure of the observed spectrum very well, revealing complicated non-adiabatic effects on the spectrum. The ground state of pyrazolyl-d_3 is $^2A_2$, and the electron affinity is 2.934 $\pm$ 0.006 eV. The first excited state is $^2B_1$, with a term energy of 32 $\pm$ 1 meV. While the stationary points of the $\tilde{X}^2A_2$ and $\tilde{A}^2B_1$ states are minima, that of $\tilde{B}^2B_2$ state is a saddle point as a result of the pseudo-Jahn-Teller interactions with the other two states. The topology of the model potential energy surfaces is discussed. Supported by NSF and AFOSR.