

THE CYCLOPENTADIENYL RADICAL REVISITED: THE EFFECTS OF ASYMMETRIC DEUTERATION OF JAHN-TELLER MOLECULES

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Asymmetric deuteration of Jahn-Teller active molecules partially lifts the vibronic degeneracy and hence provides a unique approach to understanding the Jahn-Teller effect. Previously, a spectroscopic model was proposed and used to simulate the spectra of the asymmetrically deuterated isotopomers of the methoxy radical.^{ab} The same model has been implemented and successfully simulated the previously reported high-resolution laser-induced fluorescence (LIF) spectra of the asymmetrically deuterated cyclopentadienyl radical (C₅H₄D and C₅HD₄).^c A joint fitting of the transitions from both of the zero-point levels of the $\tilde{X}^2E'_1$ ground electronic state, split by the asymmetric deuteration, to the $\tilde{A}^2A''_2$ state yields one set of molecular constants for both levels, which, when combined with molecular constants of C₅H₅ and C₅D₅, can be used to determine the molecular geometry and magnitude of the Jahn-Teller distortion. The main goal of this new investigation is to resolve the discrepancy between the experimentally determined and the ab initio calculated Jahn-Teller distortion.^d In addition, a theoretic model is proposed to quantitatively reproduce the splitting of the zero-point level due to the asymmetric deuteration and zero-point energies for the Jahn-Teller distorted structures around the conical intersection.

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