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 (C_5H_4D and C_5HD_4).[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 C_5H_5 and C_5D_5, 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.

[a] D. G. Melnik, J. Liu, R. F. Curl, and T. A. Miller, *Mol. Phys.* **105**, 529 (2007).
[b] D. G. Melnik, J. Liu, M.-W. Chen, T. A. Miller, and R. F. Curl, *J. Chem. Phys.* **135**, 094310 (2011)
[c] L. Yu, D.W. Cullin, J.M. Williamson, and T.A. Miller, *J. Chem. Phys.* **98**, 2682 (1993).
[d] M. J. Bearpark, M. A. Robb, and N. Yamamoto, *Spectrochim. Acta Part A* **55**, 639 (1999).