QUANTIFYING THE EFFECTS OF HIGHER ORDER JAHN-TELLER COUPLING TERMS ON A QUADRATIC JAHN-TELLER HAMILTONIAN IN THE CASE OF NO_3 AND Li_3.

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The Jahn-Teller (JT) effect represents an enormous complication in the understanding of many molecules. We have been able to assign $\sim$20 vibronic bands in the $\tilde{A}^2 E'' \leftarrow \tilde{X}^2 A_2'$ transition of NO_3 and determine the linear and quadratic JT coupling terms for ν_3 and ν_4, indicating strong and weak JT coupling along these modes respectively. It was found that the experimental results quantitatively disagree with ones determined from a vibronic Hamiltonian based on high-level *ab-initio* theory.[a] Typical analyses of experimental data use the quadratic JT Hamiltonian because limited measured levels tend to allow fitting only to coupling terms up to quadratic JT coupling. Hence, these analyses may neglect key contributions from cubic and quartic terms. To quantify this limitation, we have fit artificial spectra calculated with up to fourth order terms in the potential using a quadratic JT Hamiltonian and analyzed the results. The parameters chosen for this analysis are determined from *ab-initio* potentials for the $\tilde{A}$ state of NO_3 and $\tilde{X}$ state of Li_3 to gain further insight on these molecules. Our initial results concerning the limitations of the quadratic JT Hamiltonian will be presented.

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[a]T. Codd, M.-W. Chen, M. Roudjane, J. F. Stanton, and T. A. Miller. Jet cooled cavity ringdown spectroscopy of the $\tilde{A}^2 E'' \leftarrow \tilde{X}^2 A_2'$ Transition of the NO_3 Radical. *J. Chem. Phys.*, 142:184305, 2015