THE JAHN-TELLER EFFECT IN NO_3: SHEDDING NEW LIGHT ON THE DARK $\widetilde{A}\,^2E''$ STATE

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The Jahn-Teller Effect in the lowest excited states of the nitrate radical NO_3 remains poorly understood. In this paper, we examine the first excited state, $\widetilde{A}\,^2E''$, in a joint experimental and theoretical study. The forbidden $\widetilde{A}\,^2E'' \leftarrow \widetilde{X}\,^2A_2'$ transition is recorded by Near Infrared Cavity Ringdown Spectroscopy (CRDS) at medium resolution from 6000 to >10,000 cm^{-1}, extending and refining our preliminary results. We observe over 30 major vibronic bands, most with resolvable rotational structure. Tentative assignments are made on the basis of high level EOMIP-CCSD(T) calculations of the vibronic Hamiltonian, which includes up to quartic terms. Our results indicate that the $\widetilde{A}$ state undergoes static Jahn-Teller distortion, with strong vibronic coupling among both degenerate modes and the symmetric stretch. The Jahn-Teller effect in NO_3 appears to be complex and unusual, and remains a difficult but fascinating challenge.