NIR OFF-AXIS ICOS SPECTRUM OF THE NITRATE RADICAL : DOES THE VIBRATIONLESS A^2E'' STATE OF NO_3 UNDERGO STATIC JAHN-TELLER DISTORTION?

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The Jahn-Teller effect in the first two excited states of NO_3 is poorly understood. There is increasing evidence for relatively strong Jahn-Teller and Pseudo-Jahn-Teller couplings in the $\tilde{A}^2E''$ and $\tilde{B}^2E'$ states, suggesting that these states cannot be described by conventional Jahn-Teller hamiltonians. Our previous moderate resolution spectra of the forbidden $\tilde{A}^2E'' \leftarrow \tilde{X}^2A_2'$ transition revealed further evidence of strong Jahn-Teller interactions, but could not establish if the upper state exhibited static Jahn-Teller distortion. The origin band is strictly forbidden by Herzberg-Teller selection rules, and the 0^0 level can only be accessed via the weak 4_1^0 hot band. Contour analysis of the partially resolved rotational structure could not definitively establish whether the zero-point averaged geometry has D_{3h} or C_{2v} symmetry. We report the first rotationally resolved spectrum of the 4_1^0 vibronic band of NO_3 recorded by diode laser spectroscopy, using off-axis Integrated Cavity Output Spectroscopy (ICOS).