ANALYSIS OF THE ROTATIONALLY RESOLVED, NON-DEGENERATE ($a_1''$) AND DEGENERATE ($e'$) VIBRONIC BANDS IN THE $\tilde{A}^2E'' \leftarrow \tilde{X}^2A_2'$ TRANSITION OF $NO_3$.

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The magnitude of the Jahn-Teller (JT) effect in $NO_3$ has been the subject of considerable research in our group and other groups around the world. The rotational contour of the $4_0^1$ vibronic band was first described by Hirota and coworkers using an oblate symmetric top.[a] Deev *et al.* argued that an asymmetric top was required to describe the $2_0^1$ band, although their spectrum was not completely rotationally resolved.[b] These discrepancies suggest that a rotational analysis will provide considerable experimental information on the geometry of $NO_3$. Our group has collected high-resolution, rotationally resolved spectra of the vibronic $\tilde{A}^2E'' \leftarrow \tilde{X}^2A_2'$ transitions. We have completed analysis of the $3_0^1$ and $3_0^14_0^1$ parallel bands with $a_1''$ symmetry by using an oblate symmetric top with spin-rotation and centrifugal distortions. Several other parallel bands are now also reasonably understood. This analysis is consistent with a $D_{3h}$ geometry for $NO_3$. In order to analyze the perpendicular bands with $e'$ symmetry, we have adapted the oblate symmetric top Hamiltonian from the previous analysis to include spin-orbit coupling, coriolis coupling, and Watson Terms (JT distortions) that allow the oblate symmetric top Hamiltonian to transition continuously to the distorted limit of $C_{2v}$ symmetry. Preliminary analysis of the $2_0^1$ and $2_0^14_0^2$ bands has shown generally good agreement between model and experimental spectra. Our results indicate only modest JT distortions, although we do find evidence of multiple perturbations between these bands and high vibrational levels of the $\tilde{X}$ state. We will present our adapted Hamiltonian and the analysis of the $3_0^1$, $3_0^14_0^1$, $2_0^1$, and $2_0^14_0^2$ bands.

[a] E. Hirota, T. Ishiwata, K. Kawaguchi, M. Fujitake, N. Ohashi, and I. Tanaka. Near-infrared band of the nitrate radical $NO_3$ observed by diode laser spectroscopy. *J. Chem. Phys.*, 107:2829, 1997.

[b] A. Deev, J. Sommar, and M. Okumura. Cavity Ringdown Spectrum of the Forbidden $\tilde{A}^2E'' \leftarrow \tilde{X}^2A_2'$ Transition of $NO_3$: Evidence for static Jahn-Teller Distortion in the $\tilde{A}$ State. *J. Chem. Phys.*, 122:224305, 2005.