

ANALYSIS OF ROTATIONALLY RESOLVED SPECTRA TO NON-DEGENERATE ( $a_1''$ ) UPPER-STATE VIBRONIC LEVELS IN THE  $\tilde{A}^2E'' - \tilde{X}^2A_2'$  ELECTRONIC TRANSITION OF  $\text{NO}_3$

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The vibronic structure of the  $\tilde{A} - \tilde{X}$  electronic spectrum of  $\text{NO}_3$  has been observed using both room-temperature and jet-cooled samples. A recent analysis of this structure is consistent with the Jahn-Teller effect (JTE) in the  $e' \nu_3$  vibrational mode (N-O stretch) being quite strong while the JTE in the  $e' \nu_4$  mode (O-N-O bend) is rather weak. Electronic structure calculations qualitatively predict these results but the calculated magnitude of the JTE is quantitatively inconsistent with the spectral analysis.

Rotationally resolved spectra have been obtained for over a dozen vibronic bands of the  $\tilde{A} - \tilde{X}$  electronic transition in  $\text{NO}_3$ . An analysis of these spectra should provide considerably more experimental information about the JTE in the  $\tilde{A}$  state of  $\text{NO}_3$  as the rotational structure should be quite sensitive to the geometric distortion of the molecule due to the JTE. This talk will focus upon the parallel bands, which terminate on  $\tilde{A}$  state levels of  $a_1''$  vibronic symmetry, which were the subject of a preliminary analysis reported at this meeting in 2014. We have now recorded the rotational structure of over a half-dozen parallel bands and have completed analysis on the  $3_0^1$  and  $3_0^1 4_0^1$  transitions with several other bands being reasonably well understood. Two general conclusions emerge from this work. (i) All the spectral bands show evidence of perturbations which can reasonably be assumed to result from interactions of the observed  $\tilde{A}$  state levels with high vibrational levels of the  $\tilde{X}$  state. The perturbations range from severe in some bands to quite modest in others. (ii) Analyses of observed spectra, insofar as the perturbations permit, have all been performed with an oblate symmetric top model including only additional spin-rotation effects. This result is, of course, consistent with an effective, undistorted geometry for  $\text{NO}_3$  of  $D_{3h}$  symmetry on the rotational timescale.