HIGH RESOLUTION CAVITY RING DOWN SPECTROSCOPY OF THE 3_0^1 and $3_0^1\ 4_0^1$ BANDS OF THE $\tilde{A}^2\mathrm{E}''$ STATE OF NO_3 RADICAL

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The NO_3 radical is expected to exhibit a Jahn-Teller (JT) effect in its degenerate $\tilde{A}^2\mathrm{E}''$ electronic state.[a] In the $\tilde{A}$ state there are two JT active modes, ν_3 and ν_4 (e$'$ stretch and in-plane bend respectively). Theoretical work has predicted that the JT effect in the $\tilde{A}$ state should be quite strong and approach the static case where the molecule is permanently distorted to a lower symmetry geometry. A more comprehensive understanding of its structure can be achieved using high resolution rotationally resolved absorption spectroscopy of its different vibronic bands. The high resolution absorption spectra of 3_0^1 and $3_0^1\ 4_0^1$ vibronic bands of the $\tilde{A}\ ^2\mathrm{E}''$ excited state of NO_3 have been successfully recorded for the first time using our jet cooled cavity ring down apparatus. These parallel bands are vibronically allowed transitions and shows the same contour. An oblate symmetric top model Hamiltonian including both centrifugal distortion and spin rotation terms is used to analyze the spectrum. The rotational analysis of this band, supported by combination differences, demonstrate the existence of doubled lines as were observed for 4_0^n (n=1,3) bands.[b]

[a] E. Hirota, T. Ishiwata, K. Kawaguchi, M. Fujitake, N. Ohashi, and I. Tanaka, *J. Chem. Phys.*, **107**, 2829, 1997.

[b] Roudjane, M. et al. 67th OSU International Symposium on Molecular Spectroscopy, The Ohio State University, Columbus, Ohio, 2011, talk TI-03.