ROVIBRONIC ANALYSIS OF THE $e'$ BANDS IN THE $\tilde{A}^2E''$ STATE OF NO$_3$ RADICAL

HENRY TRAN, TERRANCE JOSEPH CODD, DMITRY G. MELNIK, MOURAD ROUDJANE, TERRY A. MILLER, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA.

The vibronic structure of the NO$_3$ radical has been the subject of much recent research in our group.$^a$ We have also collected several high resolution spectra of transitions to the $\tilde{A}^2E''$ state. Parallel bands, with $a''_1$ symmetry, have been satisfactorily fit using an oblate symmetric top Hamiltonian with spin rotation. Some lines were seen to be perturbed and it is likely that this is the result of random perturbations from levels originating from the ground electronic state. The perpendicular bands, which have $e'$ symmetry, are not satisfactorily described using this Hamiltonian. In particular the rotational structure of the $e'$ levels has many more transitions than in the oblate top model predicts. For this reason we have developed two different rovibronic Hamiltonians for the analysis of the vibronically degenerate levels. Both include spin-orbit, coriolis, spin-rotation, and Jahn-Teller distortion terms. However, they are derived starting from two different limiting cases. In Case 1 the Hamiltonian is built by assuming first a D$_{3h}$ configuration and then perturbations are added. Case 2 starts at the statically distorted, low symmetry geometry and introduces interactions among the vibronic levels. In the case of Jahn-Teller coupling that is neither very weak nor very strong these models should both adequately describe the observed spectra. These models and preliminary analysis of several $e'$ bands are presented.