

## Rotationally-resolved High-resolution Laser Spectroscopy and Magnetic Effect of the 662 nm Band of Nitrate Radical

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Nitrate radical ( $\text{NO}_3$ ) plays an important role in night atmospheric chemical reactions as an oxidant.  $\text{NO}_3$  has been studied by many scientists both experimentally and theoretically as reviewed by Wayne *et al* [1]. The strong absorption bands in the visible region are often used for the detection of  $\text{NO}_3$  in the environmental and in the laboratories. From the spectroscopic viewpoint, these absorption bands are assigned to the optical-allowed  $B^2E' - X^2A_2'$  electronic transition. And the most intense absorption band located at around 662 nm is assigned to the 0 - 0 band of the  $B - X$  transition. However the high-resolution fluorescence excitation spectrum of this 662 nm band was reported by Carter *et al.* [2], the rotational assignment was still remained because the observed spectrum was too complicated to be analyzed.

In this study, rotationally-resolved high-resolution fluorescence excitation spectrum of this 662 nm band of  $\text{NO}_3$  has been observed.  $\text{NO}_3$  was produced by the  $\text{N}_2\text{O}_5$  pyrolysis reaction:  $\text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2$ . The observed region was 15070 - 15145  $\text{cm}^{-1}$ . The typical linewidth of each rotational line was about 20 MHz. The absolute wavenumber of each rotational line was calibrated in the accuracy of 0.0001  $\text{cm}^{-1}$  by the simultaneous measurements of both the Doppler-free saturation spectrum of iodine and the fringe pattern of the stabilized étalon. We confirmed that the  $\text{NO}_2$  signal is negligibly small comparing to the  $\text{NO}_3$  signal in this region, from the observation of fluorescence excitation spectrum of  $\text{NO}_2$ .

More than 3000 rotational lines of  $\text{NO}_3$  were observed in the observed region, and they seemed to have less regularity. This complicated rotational structure indicates that the  $B$  ( $v' = 0$ ) state interacts with other vibronic state(s). The rotational assignment was difficult because of this complexity. However, we found many rotational line pairs with the interval of about 0.0246  $\text{cm}^{-1}$ . This interval is the same amount with the spin-rotation splitting of the  $X^2A_2'$  ( $v'' = 0, K'' = 0, N'' = 1$ ) level (i.e.  $J'' = 0.5$  and  $J'' = 1.5$  levels) [3]. From the selection rules of the  $B - X$  transition:  $\Delta K = \pm 1, \Delta J = 0, \pm 1$ , the possible rotational assignments of these pairs are  $B^2E'_{3/2}$  ( $J' = 1.5$ )  $\leftarrow X^2A_2'$  ( $N'' = 1$ ),  $B^2E'_{1/2}$  ( $J' = 0.5$ )  $\leftarrow X^2A_2'$  ( $N'' = 1$ ), and  $B^2E'_{1/2}$  ( $J' = 1.5$ )  $\leftarrow X^2A_2'$  ( $N'' = 1$ ). To assign the pairs with the interval of 0.0246  $\text{cm}^{-1}$  clearly, magnetic effect up to 360 Gauss was also observed. From the detailed analysis of the observed Zeeman spectra, we unambiguously assigned a part of the rotational lines to  $B^2E'_{3/2}$  ( $J' = 1.5$ )  $\leftarrow X^2A_2'$  ( $N'' = 1$ ) transitions and  $B^2E'_{1/2}$  ( $J' = 0.5$ )  $\leftarrow X^2A_2'$  ( $N'' = 1$ ) transitions for the first time. From the density of these transitions, the complicated structure of the 662 nm band seems to mainly owe to the vibronic interactions with the dark  $A^2E''$  state through  $a_2''$  symmetric vibrational mode. Additionally, the electronic spin  $g$  factor in the ground state was determined to 2.0215(4).

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