High-resolution laser spectroscopy and Zeeman effect of nitrate radical

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1. Introduction

The nitrate radical (NO_3) is one of the important intermediate species in various chemical reactions involving nitrogen oxides and ozone [1]. In the ancient time the NO_3 was identified by a significant visible absorption, and this absorption system is now well known to correspond to an optically allowed $B\ ^2E' \leftarrow X\ ^2A_2'$ electronic transition. The $0 - 0$ band of the $B - X$ transition is the strongest band in intensity, which is located at 15100 cm^{-1}, and some bands corresponding to the transitions to the vibrationally excited states lie in $15850 - 16100$ cm^{-1} region.

The NO_3 is regarded as one of the important models for understanding the intra-molecular interactions in polyatomic radicals; thus, we have investigated the $B - X$ transition of the NO_3 by applying rotationally-resolved high-resolution laser spectroscopic methods [2-4]. In this talk, we summarize our studies of the $0 - 0$ bands of the $^{14}NO_3$ and $^{15}NO_3$, and also we report the progress of the analysis of the transitions to the vibrationally excited states.

2. Experimental

Dinitrogen pentoxide (N_2O_5) was employed as a precursor of the NO_3, and the NO_3 was generated by the pyrolysis reaction of the N_2O_5: $N_2O_5 \rightarrow NO_3 + NO_2$ after jet-expanding the mixture of N_2O_5 vapor and helium gas into a high-vacuum chamber through a pulsed nozzle. The sample gas was shaped into a molecular beam with mechanical apertures. A single-mode ring dye laser (Coherent, CR699-29) pumped by a Nd: YVO_4 laser (Coherent, Verdi V-10) was used as a light source. The molecular beam was crossed with the dye laser beam at the right angles to reduce the Doppler width, and we observed rotationally-resolved laser-induced fluorescence (LIF) spectra. The linewidth of the rotational lines was typically 25 MHz, which is mainly the residual Doppler width. The absolute wavenumbers of the signals were calibrated to the accuracy of 0.0001 cm^{-1} by the simultaneous measurements of the fringe patterns of a cavity-length-stabilized etalon and Doppler-free saturation spectra of molecular iodine. The contamination of the NO_2 to the NO_3 spectrum was unavoidable in our experimental setup; thus, we observed the LIF spectra of the NO_2 to distinguish the NO_3 signals from the NO_2 signals.

3. The $0 - 0$ band of the $^{14}NO_3$ isotopologue [2,4]

More than 3000 rotational lines with less rotational regularity were found in the observed $15070 - 15145$ cm^{-1} region. Based on the NO_2 experiment the contamination of the NO_2 signals was confirmed to be negligible in this energy region. In the observed spectrum remarkable strong line pairs with energy spacing of 0.0248 cm^{-1} were found. This spacing is the same in magnitude with the spin-rotation splitting of the $X\ ^2A_2'$ ($v'' = 0$, $k'' = 0$, $N'' = 1$) level, where N is the quantum number of the total angular momentum excluding the electronic spin, and k is that of the projection of N along the molecular-fixed z axis. Then we found that the $B\ ^2E'$ state is described well in Hund's case (a) and the spin-orbit interaction splits this state into the $^2E'_{3/2}$ and the $^2E'_{1/2}$, because if this state is described in Hund's case (b) this 0.0248 cm^{-1} spacing is not detected directly due to the selection rule $F_1 \leftrightarrow F_1$ and $F_2 \leftrightarrow F_2$. Based on the selection rules $\Delta k = +1$, $\Delta J = 0, \pm 1$, the line pairs with the 0.0248 cm^{-1} spacing

should be assigned as the transitions to the $^2E'_{3/2}$ ($P' = 1.5$, $J' = 1.5$), $^2E'_{1/2}$ ($P' = 0.5$, $J' = 0.5$) or $^2E'_{1/2}$ ($P' = 0.5$, $J' = 1.5$) level, where J is the quantum number of the total angular momentum and P is that of the projection of $\boldsymbol{J}$ along the z axis. We observed the three types of Zeeman splitting up to 360 G with a pair of solenoid to distinguish these three types of transitions from each other. Finally, we identified seven transitions to the $^2E'_{3/2}$ ($P' = 1.5$, $J' = 1.5$) and 15 transitions to the $^2E'_{1/2}$ ($P' = 0.5$, $J' = 0.5$). From the density of the excited states we concluded that the B $^2E'$ state interacts vibronically with the dark A $^2E''$ state via the e′ type (asymmetric stretching and in-plane bending) vibrational modes. The effective spin-orbit interaction constant was estimated to be –21 cm^{-1}, based on the energy spacing of the averaged transition energies to the $^2E'_{3/2}$ (15100 cm^{-1}) and the $^2E'_{1/2}$ (15121 cm^{-1}).

In order to extend the assignment of rovibronic transitions to larger quantum numbers, we re-analyzed our high-resolution spectrum mainly based on the ground state combination differences. Owing to the selection rules $\Delta k = +1$, $\Delta J = 0, \pm 1$, the set of six rotational lines $^rP_{/k''/}(J' + 1)_{F'2}$, $^rP_{/k''/}(J' + 1)_{F'1}$, $^rQ_{/k''/}(J')_{F'2}$, $^rQ_{/k''/}(J')_{F'1}$, $^rR_{/k''/}(J' - 1)_{F'2}$, and $^rR_{/k''/}(J' - 1)_{F'1}$, which share an upper ($k'$, J') level, should be identified. We made rotational assignments for 162 lines (27 six-line sets) up to $|k''| = 15$, $J' = 18.5$. The molecular constants of the B $^2E'_{3/2}$ state were roughly estimated as $B = 0.49(4)$ cm^{-1}, $C = 0.22(3)$ cm^{-1}, and $T_0 = 15099(8)$ cm^{-1}. On the other hand, those of the B $^2E'_{1/2}$ state were roughly estimated as $B = 0.49(3)$ cm^{-1}, $C = 0.28(2)$ cm^{-1}, and $T_0 = 15110(5)$ cm^{-1}.

4. The 0 – 0 band of the $^{15}NO_3$ isotopologue [3]

We observed the rotationally-resolved LIF spectrum of the $^{15}NO_3$ in 15080 – 15103 cm^{-1} region, where about 200 strong lines and several thousand weak lines were found. We assumed that the $^{15}NO_2$ contamination is negligible, and the excited B $^2E'$ state can be described in Hund's case (a). We identified two transitions to the $^2E'_{3/2}$ spin-orbit component, whereas six transitions to the $^2E'_{1/2}$. For the intrinsic B $^2E'_{1/2}$ state we successfully made the rotational assignments of the $k = 1 \leftarrow 0$ stack up to $J' = 10.5$, and the molecular constants of this upper state were determined as $T_0 = 15098.20(4)$ cm^{-1}, $B = 0.4282(7)$ cm^{-1}, and $D_J = 4 \times 10^{-4}$ cm^{-1}. The spin-orbit interaction constant of the B $^2E'$ state was estimated to be –12 cm^{-1} as the lower limit in magnitude.

5. The vibrationally excited B $^2E'$ states of the $^{14}NO_3$ isotopologue

The vibronic band located at around 15900 cm^{-1} was assigned as the 4^2_0 band of the $B – X$ transition [5]. The high-resolution spectrum in 15860 – 15920 cm^{-1} has been observed, and we are in the progress of analyzing this spectrum. We identified many strong line pairs with the 0.0248 cm^{-1} spacing corresponding to the transitions to the levels with the smallest quantum numbers of both the $^2E'_{3/2}$ and $^2E'_{1/2}$ spin-orbit components. These line pairs are not random in distribution but consisting of band groups, and we found that these $^2E'_{3/2}$ and $^2E'_{1/2}$ groups appear alternately.

[1] R. P. Wayne, I. Barnes, P. Biggs, J. P. Burrows, C. E. Canosa-Mas, J. Hjorth, G. Le Bras, G. K. Woortgat, D. Perner, G. Poulet, G. Restelli, H. Sidebottom, Atmos. Environ. **25A**, 1 (1991).
[2] K. Tada, W. Kashihara, M. Baba, T. Ishiwata, E. Hirota, and S. Kasahara, J. Chem. Phys. **141**, 184307 (2014).
[3] K. Tada, K. Teramoto, T. Ishiwata, E. Hirota, and S. Kasahara, J. Chem. Phys. **142**, 114302 (2015).
[4] K. Tada, T. Ishiwata, E. Hirota, and S. Kasahara, J. Mol. Spectrosc. **321**, 23 (2016).
[5] M. Fukushima, and T. Ishiwata, 67th Int. Symp. Mol. Spectrsc. TI06 (2012).