# Analyses of the Infrared Absorption Bands of <sup>15</sup>NO<sub>3</sub> in the 1850–3150 cm<sup>-1</sup> Region

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We have observed the infrared spectrum of <sup>15</sup>NO<sub>3</sub> by a high resolution Fourier transform infrared (FT-IR) spectrometer using the reaction of F atoms with H<sup>15</sup>NO<sub>3</sub>. Five  ${}^{2}E'-{}^{2}A_{2}'$  bands are identified in the 1850–3150 cm<sup>-1</sup> region. The rotational analyses indicate that these bands have the lower state in common, which coincides with the ground state of planar  $D_{3h}$  symmetry. The upper  ${}^{2}E'$  states more or less suffer from perturbations by close-lying dark states. Among them, those of the 2004, 2128, and 2492 cm<sup>-1</sup> bands are analyzed to determine molecular parameters in these states by fixing the ground-state constants to those derived by a combination difference method. The spin—orbit and Coriolis coupling constants in the  ${}^{2}E'$  states are substantially different for different vibronic states. The vibrational assignments of NO<sub>3</sub> in the ground electronic state are discussed using experimental data heretofore available, supplemented by those obtained by the present study.

## 1. Introduction

The nitrate radical (NO<sub>3</sub>) is one of the chemical intermediates that play important roles in chemical transformation in the Earth's atmosphere.<sup>1–3</sup> Atmospheric NO<sub>3</sub> is predominantly formed by the reaction

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{1}$$

During the daytime, NO<sub>3</sub> is rapidly photolyzed by sunlight and is known to participate in the reaction system, which reduces the ozone concentration in the stratosphere. On the other hand, NO<sub>3</sub> persists at night and works as the most important oxidizing species in the troposphere, in place of OH during the daytime. The NO<sub>3</sub> radicals react with certain organic compounds, typically by hydrogen abstraction or by addition to an unsaturated bond, and contribute to the chemical processes giving acid rain and toxic compounds in the atmosphere, i.e., to air pollution by artificial NO<sub>x</sub> emissions.

To detect NO<sub>3</sub> in an ambient air and laboratories, it is usual to use the visible electronic transition which has been known since the 19th century. This system consists of about 20 diffuse bands in the 480–680 nm range, and its strong absorption centered at ~662 nm is ascribed to the (0–0) band.<sup>4,5</sup> This electronic transition is historically labeled as  $\tilde{B}^2E'-\tilde{X}^2A_2'$  in accord with the Walsh diagram,<sup>6</sup> originating from qualitative theoretical consideration, but this assignment was not based on experimental evidence even for the ground state until recently.

The spectroscopic studies on NO<sub>3</sub> were initiated with the laser spectroscopic observations carried out about a quarter century ago; Ishiwata et al.<sup>7</sup> and Nelson et al.<sup>8</sup> succeeded independently in observing laser induced fluorescence and dispersed fluorescence spectra of the  $\tilde{B}^2 E' - \tilde{X}^2 A_2'$  transition. The spectral data obtained by the two groups were almost identical, but Ishiwata et al. supposed the ground-state structure of NO<sub>3</sub> to be of  $D_{3h}$  symmetry in analyzing the dispersed fluorescence spectra, whereas Nelson et al. supposed it to be of  $C_{2\nu}$ . Ishiwata et al. reported the frequencies of three vibrational modes in the ground electronic state that are active in fluorescence:  $\nu_1$  (a<sub>1</sub>': symmetric N–O stretch),  $\nu_3$  (e': degenerate N–O stretch), and  $\nu_4$  (e': degenerate ONO deformation). Ishiwata et al.<sup>9</sup> and Kawaguchi et al.<sup>10</sup> applied infrared diode laser spectroscopy to a band around 1492 cm<sup>-1</sup> and unambiguously assigned the ground electronic state to be of <sup>2</sup>A<sub>2</sub>' symmetry with a planar  $D_{3h}$ structure from the rotational analysis. They also showed that the upper state of the 1492 cm<sup>-1</sup> band was an E' vibronic state, consistent with the assignment of the band to the  $\nu_3$  fundamental. The E' vibronic state was subject to a few anomalies arising from the vibronic coupling with the  $\tilde{B}^2E'$ , which was discussed by Hirota et al.<sup>11</sup>

Friedl and Sander<sup>12</sup> confirmed our observation of the 1492 cm<sup>-1</sup> band by Fourier transform infrared spectroscopy, and newly found the  $\nu_2$  (a<sub>2</sub>": out-of-plane bending) band at 762 cm<sup>-1</sup>. Weaver et al.<sup>13</sup> reported the photoelectron spectra of NO<sub>3</sub><sup>-</sup>. Their analysis indicated that the ground electronic state of NO<sub>3</sub> had a  $D_{3h}$  equilibrium geometry and was vibronically coupled to the  $\tilde{B}^{2}E'$  state through the  $\nu_{4}$  mode. We extended the analysis from 1500 to 3000 cm<sup>-1</sup> by infrared diode laser spectroscopy and Fourier transform infrared spectroscopy and identified about 10 bands.<sup>14–16</sup> Some of them were too complicated to analyze, perhaps because of perturbations by close-lying dark states. The bands analyzed were all found to be due to perpendicular transitions of the E-A type with the  $\tilde{X}^2A_2'$  state as the lower state in common. We noticed that the E' vibronic levels in the region between 2000 and 3000 cm<sup>-1</sup> were difficult to simply represent in terms of overtone and/or combination states of the four normal modes, and thus only tentative assignments have been given for the observed bands.

A number of ab initio calculation studies have been carried out on NO<sub>3</sub> concerning the equilibrium geometry and harmonic frequencies for the  $\tilde{X}^2A_2'$  ground state.<sup>17</sup> However, the results so far obtained were not conclusive as to the explanation for anomalies in the vibronic energy levels in the  $\tilde{X}^2A_2'$  state. In

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relation to this problem, Stanton<sup>18</sup> recently proposed a reassignment of the vibrational state lying at 1492 cm<sup>-1</sup> to  $v_1 + v_4$ using the model Hamiltonian approach developed by Köppel et al.,<sup>19</sup> and interpreted the bands in the fluorescence spectrum and the photoelectron spectra of NO<sub>3</sub><sup>-</sup> on the basis of a new assignment of  $v_3$  to be ~1000 cm<sup>-1</sup>.

More recently, Jacox and Thompson<sup>20</sup> observed the infrared spectra of NO<sub>3</sub> and its isotopic species trapped in sold neon in the 700–3000 cm<sup>-1</sup> range. Their study confirmed the bands observed in the gas phase and, in addition, identified some weak ones that were not detected in previous studies. A weak band thus found at 1412.5 cm<sup>-1</sup> was more reasonable to assign to  $v_1 + v_4$  in view of the observed intensities and isotope shifts, and the 1492 cm<sup>-1</sup> band to  $v_3 + v_4$ .<sup>21</sup> Beckers et al.<sup>22</sup> observed the  $v_4$  fundamental band in Ne matrix and gave a tentative assignment of the vibronic bands on the basis of  $v_3 \sim 1100$  cm<sup>-1</sup> by following the reassignment of the 1492 cm<sup>-1</sup> band. Stanton<sup>23</sup> studied the infrared spectrum of NO<sub>3</sub> by using the equation-of-motion coupled-cluster method, and the  $v_3$  fundamental mode was calculated to lie at 1067 cm<sup>-1</sup>.

Under these circumstances, we have restarted a program of the study on the NO<sub>3</sub> radical using high-resolution spectroscopy, by focusing attention to the effects of vibronic interactions on the ground state, including primarily the vibrational reassignment of  $\nu_3$  proposed by Stanton. The present paper describes the first report of such study on the <sup>15</sup>N isotopic species of NO<sub>3</sub>.

#### 2. Experimental Section

The infrared absorption spectra of  ${}^{15}NO_3$  were recorded at 0.008 cm<sup>-1</sup> resolution using a Fourier- transform spectrometer (Bruker IFS 120 HR) at Okayama University. An absorption cell equipped with a White-type multireflection mirror system, 14.2 cm in inner diameter and 150 cm in length, was employed, and the effective path length was set to be 24 m.

We generated <sup>15</sup>NO<sub>3</sub> by the reaction of  $F + H^{15}NO_3$ . Fluorine atoms were generated by a microwave discharge in F<sub>2</sub> diluted to 1% by He. We produced H<sup>15</sup>NO<sub>3</sub> by the reaction of Na<sup>15</sup>NO<sub>3</sub> (99.8% <sup>15</sup>N, obtained from Shoko Co. Ltd.) with H<sub>2</sub>SO<sub>4</sub> and purified it by vacuum distillation. The experimental conditions were typically 70 mTorr of H<sup>15</sup>NO<sub>3</sub> at a total pressure of 1.5 Torr.

# 3. Results

a. Spectral Features. We identify five vibrational bands of <sup>15</sup>NO<sub>3</sub> in the 1850–3150 cm<sup>-1</sup> range. They are all perpendicular transitions of the  ${}^{2}E^{-2}A$  type, and their features resemble those previously observed for <sup>14</sup>NO<sub>3</sub>.<sup>9,10,14-16</sup> The spectra clearly show a characteristic series of doublets attributed to the  ${}^{r}Q_{0}(N)$  branch transitions lying near the band origin, and much stronger  $^{p}P$ and  $^{r}R$  branch transitions at lower and higher frequencies than  $^{r}Q_{0}(N)$ , respectively. Among the observed five bands, three at 2004, 2128, and 2492  $\text{cm}^{-1}$  are rotationally analyzed in detail (all the transition frequencies observed for the three bands are listed in the tables in the Supporting Information), while the remaining two bands at 1900 and 2868 cm<sup>-1</sup> suffer from strong perturbations in the upper states, preventing us from carrying out rotational analyses. The rotational lines of these two bands are partly assigned for some smaller K and N levels, but it is difficult to extend the assignment to larger K and N levels. For the rest of the bands, we use a Hamiltonian for  $D_{3h}$  molecules without explicitly taking account of perturbations in the upper state. Some other bands, which correspond to those observed



Figure 1. *R* branch side of the spectrum of the 2004 cm<sup>-1</sup> band of <sup>15</sup>NO<sub>3</sub>.



Figure 2. Spectrum near the origin of the 2004  $cm^{-1}$  band of <sup>15</sup>NO<sub>3</sub>.

for  $^{14}NO_3$  in the 2200–2400 cm $^{-1}$  region, either are too weak or are missing due to the overlap of absorption bands of  $N_2O_5$  and HNO\_3.

Figure 1 shows an example of the spectra observed for the *R*-branch side of the 2004 cm<sup>-1</sup> band. The observed lines appear with *K* numbers equal to 0, 3, 6, 9, 12, ...; i.e., K = 3n (n = integer) levels only occur. This observation indicates that three oxygen atoms with zero nuclear spin are equivalent in the molecule, supporting the presence of a 3-fold axis. On the other hand, as shown in Figure 2, the  $'Q_0(N)$  transitions observed near the band origin show that the *N* quantum number is limited to 1, 3, 5, ...; that is, only odd *N* levels occur. Two oxygen atoms are therefore equivalent with respect to a 2-fold axis, which is perpendicular to the 3-fold axis. These observations establish a planar  $D_{3h}$  structure of <sup>15</sup>NO<sub>3</sub> and show that the ground state is the <sup>2</sup>A<sub>2</sub>' electronic state as is the case with <sup>14</sup>NO<sub>3</sub> reported previously.<sup>9</sup>

**b.** Ground State. In analyzing the vibrational bands, we fix the molecular constants of the ground state determined from the combination differences, which are formed either from  ${}^{r}R$  and  ${}^{r}Q$  branch transitions or from  ${}^{p}Q$  and  ${}^{p}P$  transitions, as described below:

$$\Delta''(N,K) = F''(N+1,K) - F''(N,K)$$
  
=  ${}^{r}R_{K}(N) - {}^{r}Q_{K}(N+1)$  (2)  
=  ${}^{p}Q_{K}(N) - {}^{p}P_{K}(N+1)$ 

There are several reasons for carrying out such an analysis. First, the upper E' vibronic states more or less suffer from

TABLE 1: Molecular Constants of NO<sub>3</sub> in the  $^2A_2^\prime$  Ground State  $(cm^{-1})^\alpha$ 

	${}^{15}NO_{3}{}^{b}$	$^{14}\text{NO}_3{}^c$
В	0.4586150(68)	0.4585485(63)
$D_N$	$1.093(13) \times 10^{-6}$	$1.113(12) \times 10^{-6}$
$D_{NK}$	$-2.063(40) \times 10^{-6}$	$-2.121(27) \times 10^{-6}$
$\varepsilon_{bb}$	-0.01640(14)	-0.01649(13)

<sup>*a*</sup> Values in parentheses denote one standard deviation. The planarity condition is assumed: C = B/2 and  $D_K = -(2D_N + 3D_{NK})/4$ . <sup>*b*</sup> Present study. <sup>*c*</sup> Reference 16.

perturbations by close-lying dark states. These perturbations make it difficult to fit the observed spectral line frequencies within the experimental accuracy without taking into account the effects of perturbations. Furthermore, the perturbations in the upper E' states occur in different ways for different vibronic states, which may make the molecular constants of the ground state inconsistent among band-by-band analyses. Under these circumstances, it is quite useful to analyze the lower state only without being affected by perturbations in the upper states. Second, the analyses using combination differences lead to unambiguous assignment for the two spin components; the spectral lines of NO<sub>3</sub> are split into two spin components and it is not always obvious to assign which component to  $F_1$  or  $F_2$ transitions. The transitions of these spin components are sometimes inverted in energies, and the spectra show different appearance. Third, what is more important is that the analysis based on the combination differences establishes an accurate assignment of the rotational quantum number N. Since spectral lines are congested in the energy region where the  ${}^{p}Q$  and  ${}^{r}Q$ transitions appeared, the relation shown in eq 2 is quite useful to assign these series of transitions. We thus derive 412 combination differences for the lower state from the five infrared bands under the study: 31 in the 1900 cm<sup>-1</sup> band, 132 in the  $2004 \text{ cm}^{-1}$  band, 99 in the 2128 cm<sup>-1</sup>, 97 in the 2492 cm<sup>-1</sup> band, and 53 in the 2868 cm<sup>-1</sup> band. These data are all consistent within the accuracy of the measurements, and five infrared bands observed in the present study are confirmed to have the  ${}^{2}A_{2}'$  ground state as the common lower state.

The expression for the rotational energy levels of the ground state is

$$\langle N,k,l|H_{vr}|N,k,l\rangle = BN(N+1) + (C-B)k^2 - D_N N^2 (N+1)^2 - D_{NK} N(N+1)k^2 - D_K k^4$$
(3)

where C = B/2 is assumed, in accord with a  $D_{3h}$  molecular structure. The planarity relation for the centrifugal distortion terms,  $2D_N + 3D_{NK} + 4D_K = 0$ , is also employed. The spin-rotation interaction is included in both the diagonal and off-diagonal blocks as follows:

$$\langle N,k,l,J|H_{\rm sr}|N,k,l,J\rangle = \{\varepsilon_{bb} - (\varepsilon_{bb} - \varepsilon_{cc})k^2/[N(N+1)]\} \times \{[J(J+1) - N(N+1) - S(S+1)]/2\}$$
(4)

and

$$\langle N-1, k, l, J | H_{\rm sr} | N, k, l, J \rangle =$$
  
(1/2) $(\varepsilon_{bb} - \varepsilon_{cc})(k/2N)[N^2 - k^2]^{1/2}$  (5)

The molecular constants of the ground state thus derived are summarized in Table 1. The standard deviation of fitting is 0.001 36 cm<sup>-1</sup>. The molecular constants of the <sup>15</sup>N substituted species of NO<sub>3</sub> are consistent with those derived in the normal

species containing <sup>14</sup>N.<sup>10,16</sup> The rotational constants are essentially invariant between the two species, since the nitrogen atom sits at the center of the molecule. The substitution of the nitrogen atom with its isotope will not change the moment of inertia of the radical much, as is actually found. The N–O bond length  $r_0$  is calculated to be 1.2381 Å from the ground-state rotational constant of <sup>15</sup>NO<sub>3</sub>.

The observed ground-state spin-rotation interaction constant is found to be consistent with the electronic structure of NO<sub>3</sub>;  $\varepsilon_{bb}$  is determined to be -0.016 cm<sup>-1</sup>, in good accord with that estimated using the following theoretical expression:<sup>24</sup>

$$\varepsilon_{bb} = 4A_{\rm SO} \sum_{n} \langle 0|L_b|n \rangle \langle n|BL_b|0 \rangle / (E_n - E_0) \tag{6}$$

In this expression,  $|0\rangle$  and  $|n\rangle$  denote the ground and electronically excited states, respectively,  $L_b$  represents the *b* component of the electronic orbital angular momentum, and  $E_n$  and  $E_0$  stand for the energies of the *n*th excited and the ground states, respectively. Because  $L_a$  and  $L_b$  belong to E'' symmetry, the ground state of  $A_2'$  symmetry will interact with excited states of E'' symmetry. NO<sub>3</sub> has the first excited state,  $\tilde{A}^2$ E'', at 7000 cm<sup>-1</sup> above the ground state,  $^{13,25,26}$  and the observed  $\varepsilon_{bb}$  constant leads to the spin—orbit interaction constant  $A_{SO}$  of about 60 cm<sup>-1</sup>, which is comparable to the corresponding value of O atom, 160 cm<sup>-1</sup>, and is consistent with the theoretical prediction that an unpaired electron in the ground state lies in the p orbital of the O atom lying on the molecular plane.<sup>27</sup>

The  $\varepsilon_{cc}$  constant arises from the interactions of the ground electronic state with excited states of A<sub>1</sub>" symmetry. An ab initio calculation predicts such states lying far apart, more than 60 000 cm<sup>-1</sup> above the ground electronic state.<sup>27</sup> Therefore,  $\varepsilon_{cc}$  will be negligibly small, and in fact, it is not necessary to introduce this parameter in the present analysis.

It should be pointed out that the molecular parameters for the ground state of <sup>15</sup>NO<sub>3</sub> shown in Table 1 are different from those reported in our first paper on <sup>14</sup>NO<sub>3</sub>.<sup>9</sup> The spin-rotation interaction constants,  $\varepsilon_{bb}$  and  $\varepsilon_{cc}$  reported in ref 9, in particular, differ much from the present results. The discrepancies primarily stem from our failure in analyzing the upper E' vibronic state of the 1472 cm<sup>-1</sup> band of <sup>15</sup>NO<sub>3</sub>; the previous analysis took into account the  $\varepsilon_{cc}$  spin-rotation interaction constant. But we later noticed that this  $\varepsilon_{cc}$  constant was too large compared with a theoretically expected value and should be replaced by a spin-orbit interaction term in the upper E' state, as described in the second paper on <sup>14</sup>NO<sub>3</sub>.<sup>10</sup> In the previous analysis by diode laser spectroscopy, we derived 22 combination differences for the lower state of the 1472 cm<sup>-1</sup> band of <sup>15</sup>NO<sub>3</sub>. These data spanned the ranges of K'' = 3-15 and N'' = 6-18 and were consistent with those derived in the present study from other bands. We thus confirmed that the 1472 cm<sup>-1</sup> band of <sup>15</sup>NO<sub>3</sub> also originated from a transition with the  $\tilde{X}^2 A_2'$  ground state as the lower state.

**c. Vibrationally Excited States.** The analyses of the rotational structure in the upper vibrational states were performed using a Hamiltonian appropriate for the states of vibronic E' symmetry. The diagonal term of the vibration and rotation energy is given by

$$\langle N,k,l|H_{vr}|N,k,l\rangle = T_{v} + BN(N+1) + (C - B)k^{2} - 2C\xi kl + \eta_{N}N(N+1)kl + \eta_{K}k^{3}l - D_{N}N^{2}(N+1)^{2} - D_{NK}N(N+1)k^{2} - D_{K}k^{4}$$
(7)

The off-diagonal term

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$$\langle N, k+1, l=1 | H_{vr} | N, k-1, l=-1 \rangle = (1/2)[q + q_N N(N+1)] \times \{ [N(N+1) - k(k-1)][N(N+1) - k(k+1)] \}^{1/2}$$
(8)

is included to account for the (2, 2) vibration–rotation interaction. The matrix elements of the spin-rotation interaction are identical to those of eqs 4 and 5. Furthermore, as in the case of  $^{14}NO_3$  reported previously,<sup>10</sup> the Hamiltonian includes the spin–orbit interaction matrix elements as follows:

$$\langle N,k,F_1|H_{\rm SO}|N,k,F_1\rangle = a_{\rm eff}k/2(N+1) \tag{9}$$

$$\langle N,k,F_2|H_{\rm SO}|N,k,F_2\rangle = a_{\rm eff}k/2N \tag{10}$$

$$\langle N-1, k, F_1 | H_{\rm SO} | N, k, F_2 \rangle = a_{\rm eff} (N^2 - k^2)/2N$$
 (11)

where  $a_{\text{eff}} = \langle E^{\text{ev}} | a L_z | E^{\text{ev}} \rangle$  denotes an effective spin-orbit coupling constant in the upper vibrational state.

The subband analyses for each of the K sublevels were carried out iteratively to assign the transitions in the observed spectra with fixing the molecular constants of the ground state. Since the ground-state parameters were initially unknown, assignments were facilitated by a set of constants derived for <sup>14</sup>NO<sub>3</sub> previously.<sup>16</sup> As expected, the substitution of <sup>15</sup>N isotope in the normal <sup>14</sup>NO<sub>3</sub> species did not affect the molecular parameters in the ground state, and the spectra were reasonably assigned in lower K and N levels. This analysis provided combination differences for the ground state that were sufficient enough to give its molecular constants, and we used them to calculate the ground-state constants for <sup>15</sup>NO<sub>3</sub> by a least-squares method. The subband analyses continued to extend the assignments by using this new set of constants, and additional data thus obtained provided new combination differences of the ground state to improve its molecular constants. By repeating this cycle several times, we finally assigned 651 transitions for the 2004 cm<sup>-1</sup> band, 498 for the 2128  $\text{cm}^{-1}$  band, and 511 for the 2492  $\text{cm}^{-1}$ band.

The observed lines thus assigned were fed to a total fitting program, where the ground-state constants were fixed to those listed in Table 1. In the 2000 cm<sup>-1</sup> energy region, there are several overtone or combination states that come close to the upper E' states under the study. The perturbing states were not necessarily evident by the occurrence of additional lines and/ or the level crossing, but the spectra showed apparent energy shifts in the E' upper states. The shifts generally depend largely on N, which suggests the perturbation is inhomogeneous. However, the data were in most cases insufficient to specify which lines should be included in the fit. To describe the upper states, we fitted the data using an effective Hamitonian for a degenerate vibrational state without explicitly taking into account the perturbations. The resulting parameters obviously depend on our choice of lines included but are good enough to limit the residual to 0.008 cm<sup>-1</sup>, which is close to the spectral resolution of the present study.

The upper state of the 2004 cm<sup>-1</sup> band was less perturbed than those of the other two bands at 2128 and 2492 cm<sup>-1</sup>. Even in this case, however, we could include only 441 transitions in the analysis, which corresponded to only 64.9% of the total assigned lines in the subband analysis. The situations were much worse in the other bands: 146 transitions (29.1%), and 217 transitions (39.2%) for the 2128 and 2492 cm<sup>-1</sup> bands, respectively. The transition frequencies employed for the determination of molecular constants are almost free from the perturbations, as certified by the ground-state combination differences (see the paragraph right after eqs 9–11), and allowed

TABLE 2: Molecular Constants of  ${}^{15}NO_3$  in the E' Vibronic States  $(cm^{-1})^a$ 

	$2004 \text{ cm}^{-1}$	$2128 \text{ cm}^{-1}$	$2492 \text{ cm}^{-1}$
$\nu_{00}$	2003.9849(4)	2128.5244(10)	2492.9587(6)
В	0.4534443(50)	0.454139(26)	0.454279(15)
С	0.2264397(43)	0.226500(14)	0.2265752(67)
$D_N$	$0.816(13) \times 10^{-6}$	$1.24(18) \times 10^{-6}$	$1.152(82) \times 10^{-6}$
$D_{NK}$	$-1.811(27) \times 10^{-6}$	$-2.85(28) \times 10^{-6}$	$-2.14(17) \times 10^{-6}$
$D_K$	$0.980(19) \times 10^{-6}$	$1.29(28) \times 10^{-6}$	$0.969(85) \times 10^{-6}$
$C\zeta$	-0.004217(19)	-0.022250(57)	0.018005(28)
$\eta_{\rm N}$	$-0.834(17) \times 10^{-5}$	$-4.60(12) \times 10^{-5}$	$0.289(51) \times 10^{-5}$
$\eta_K$	$0.704(18) \times 10^{-5}$	$4.29(11) \times 10^{-5}$	$-0.323(50) \times 10^{-5}$
, q	0.0037649(75)	0.00884(27)	0.000522(35)
$q_N$		$-4.44(19) \times 10^{-5}$	
$a_{\rm eff}$	0.01805(39)	0.06518(84)	0.10306(52)
$\varepsilon_{bb}$	-0.018317(27)	-0.01705(11)	-0.017031(57)
$\varepsilon_{bb} - \varepsilon_{aa}$	-0.01356(40)		-0.00917(51)
$\sigma_{\rm fit}$	0.00243	0.00362	0.00258

<sup>*a*</sup> Values in parentheses denote one standard deviation. The ground-state constants were fixed to those in Table 1.

TABLE 3: Isotope Shift of Band Origin (cm<sup>-1</sup>)

			isotope shift $(\Delta E)^{b}$	
band	$^{15}\mathrm{NO}_3{}^a$	<sup>14</sup> NO <sub>3</sub>	gas <sup>a</sup>	matrix <sup>c</sup>
1492	1472.8331(13) <sup>d</sup>	1492.3936(5) <sup>e</sup>	19.561	19.4
1927	$N.G.^{f}$	N.G.		28.1
2024	2003.9849(4)	2024.3230(8)	20.338	20.2
2155	2128.5244(10)	2155.1885(7)	26.664	26.8
2200	N.M. <sup>g</sup>	N.G.		24.3
2240	N.M.	N.G.		23.4
2380	N.M.	N.G.		
2518	2492.9587(7)	2518.7130(5)	25.754	25.6
2585	N.G.	2585.0935(10)		33.6
2900	N.G.	N.G.		27.9

<sup>*a*</sup> Present study. <sup>*b*</sup> Relative to <sup>15</sup>NO<sub>3</sub>:  $\Delta E = E_v(^{14}NO_3) - E_v(^{15}NO_3)$ . <sup>*c*</sup> Reference 20. In Ne matrix. <sup>*d*</sup> Reference 9. <sup>*e*</sup> Reference 10. <sup>*f*</sup> Not given. <sup>*g*</sup> Not measured.

us to determine molecular constants of the upper E' states, as summarized in Table 2.

d. Isotope Effect. Table 3 summarizes the origins of the vibrational bands observed for <sup>15</sup>NO<sub>3</sub>, to be compared with those of <sup>14</sup>NO<sub>3</sub>, where the correspondence of the bands between the two isotopic species is made by assuming the isotope shifts to be in the range of 20-30 cm<sup>-1</sup>. In addition, the band intensities give further information on the correspondence. For <sup>15</sup>NO<sub>3</sub>, the relative intensities of the four dominant bands at 1900, 2004, 2128, and 2492 cm<sup>-1</sup> are roughly 1:0.5:0.6:0.6, as estimated from the absorbance of the  ${}^{r}R_{6}(6)$  transition, which are very close to those of the bands of <sup>14</sup>NO<sub>3</sub>, each lying 20-30 cm<sup>-1</sup> higher than the <sup>15</sup>NO<sub>3</sub> band.<sup>16</sup> Jacox and Tompson<sup>20</sup> reported the absorption bands of <sup>14</sup>NO<sub>3</sub> and its isotopic species in Ne matrices. Although the absorption bands are shifted by matrix effects to lower frequencies by about 1 cm<sup>-1</sup>, the isotope shifts agree within  $0.2 \text{ cm}^{-1}$  with the present results in the gas phase. This observation confirms that the vibrational bands observed in the present study are all cold bands; i.e., their lower states are common: the ground vibrational state, as already established by our analyses.

Table 4 compares the Coriolis coupling and the effective spin-orbit interaction constant,  $\zeta$  and  $a_{\text{eff}}$ , derived for the E' upper vibrational states for the two isotopic species, <sup>14</sup>NO<sub>3</sub> and <sup>15</sup>NO<sub>3</sub>. These two parameters, both magnitude and sign, will reflect characteristic features of the upper E' states, and it is interesting to note that both the parameters behave in parallel to some extent but still exhibit sizable variations between the two species. From the results of the present study, we may add

TABLE 4: Summary of the Molecular Constants of the E' States

	$^{14}NO_3$		<sup>14</sup> NO <sub>3</sub> <sup>15</sup> NO <sub>3</sub>			assig	nment
band	ξ	$a_{\rm eff}{}^a$	ζ	$a_{\rm eff}{}^a$	$\Delta E^a \ ({ m cm}^{-1})$	$\mathbf{I}^b$	$\Pi^c$
1492	0.194	0.173			19.561 <sup>d</sup>	$\nu_3$	$v_3 + v_4$
1927	-0.20	-0.09			(28.1)	$\nu_3 + \nu_4$	$\nu_3 + 2\nu_4$
2024	-0.011	-0.013	-0.019	0.018	20.338	$5\nu_4$	$5\nu_4$
2155	-0.108	0.093	-0.098	0.065	26.664	$\nu_1 + 3\nu_4$	$\nu_1 + \nu_3$
2518	0.103	0.139	0.079	0.103	25.754	$\nu_1 + \nu_3$	$\nu_1 + 4\nu_4$
2585	0.116	-0.034			(33.6)	$2\nu_1 + \nu_4$	$2\nu_3 + \nu_4$

<sup>*a*</sup> In cm<sup>-1</sup>.  $\Delta E = E_v({}^{14}NO_3) - E_v({}^{15}NO_3)$ . <sup>*b*</sup> Reference 16. <sup>*c*</sup> References 18, 20, and 22. <sup>*d*</sup> References 9 and 10.

two more terms to this list: the *l*-type doubling constant *q* and the anisotropic term of the spin-rotation interaction  $\varepsilon_{bb} - \varepsilon_{aa}$ . These findings not only give the basis for the correspondence of the bands of the two isotopic species as listed in Table 4 but also provide us with invaluable information on the characteristics of the upper vibrational states leading to the vibrational assignments of these states.

### 4. Discussion

As mentioned in the Introduction, the vibrational assignment for NO<sub>3</sub> in the ground electronic state has not been established. Stanton<sup>18</sup> proposed a new assignment for the  $\nu_3$  fundamental band at around 1000 cm<sup>-1</sup>, at variance with the earlier and widely accepted position of 1492 cm<sup>-1</sup>.<sup>7,9-12</sup> We have carefully scanned the region from 800 to 1400 cm<sup>-1</sup> by Fourier transform infrared spectroscopy to detect the " $\nu_3$ " band but did not observe any band stronger than 0.1 of the 1492 cm<sup>-1</sup> band. Stanton<sup>21,23</sup> later calculated the intensity of the " $\nu_3$ " band to be extremely small (~1/600).

Stanton's proposal, if correct, requires revision of the vibrational assignment for overtone and combination bands observed in the  $1500-3150 \text{ cm}^{-1}$  region, which was tentatively made by Kawaguchi et al.<sup>16</sup> some years ago. In fact, Beckers et al.<sup>22</sup> recently reported an alternative assignment mainly based on the isotope shifts of the vibrational frequencies calculated by Stanton,<sup>23</sup> claiming that this assignment resolved all "conflicting observations". However, the isotope shifts in vibrational frequency are certainly insufficiently by themselves to fully endorse Stanton's proposal. Table 4 compares the two assignments: I (Kawaguchi et al.) and II (Beckers et al.) for the six most prominent bands in the 1400–2600 cm<sup>-1</sup>, where one modification is made for I, namely the 1927 cm<sup>-1</sup> band is assigned to  $\nu_3 + \nu_4$ .

There are two major difficulties in making vibrational assignment for NO<sub>3</sub> in the ground electronic state: vibronic interaction and vibration—rotation interaction including anharmonicity resonance. The two factors are obviously correlated to some extent. Hirota et al.<sup>11</sup> attempted to explain anomalies observed for the 1492 cm<sup>-1</sup> band in terms of vibronic interaction. One of the important findings they reported is that, when they treated the first-order and second-order vibronic interaction terms by perturbation, they found cubic anharmonic potential terms to result in the vibrational potential function. For example, when the  $\nu_3$  normal coordinate is active in the vibronic interaction, the perturbation contributes to the  $k_{333}$  cubic constant, which has been known to play an important role in the *l*-type doubling constant, a result of the vibration—rotation interaction.

It would be natural to presume that the higher the vibrational state is, the more extensive the anharmonicity mixing is, and we have thus decided to focus attention mainly to the  $1492 \text{ cm}^{-1}$  band in the present study and have critically examined the two

assignments I and II using experimental data other than the isotope shifts of the vibrational frequencies on which Beckers et al.'s discussion is mainly based. As Kawaguchi et al.<sup>10</sup> reported, two prominent anomalies appear in this band: the spin—orbit coupling term and the first-order Coriolis coupling constant. The rotational analysis of this band requires a small, but definite, spin—orbit coupling term to be included, in spite of the fact that the ground electronic state is of electronically nondegenerate A<sub>2</sub>' symmetry. The Coriolis constant may be calculated from a conventional force field to be  $\zeta \approx 0.7$ , which differs much from the observed value of  $\zeta \approx 0.2$ .

The presence of a small spin-orbit interaction constant in the upper state of the 1492  $cm^{-1}$  band is obviously ascribed to mixing of the excited electronic states of E' symmetry with this state. Hirota et al.<sup>11</sup> in fact showed that the first-order vibronic interaction term containing the  $q_3$  coordinate linearly accounted for the small spin-orbit coupling constant. This treatment is of course based upon the assignment I, and the first-order vibronic interaction matrix element of about 1139 cm<sup>-1</sup> was required to explain the small spin-orbit interaction constant of 0.173 cm<sup>-1</sup>, where the upper electronic state responsible for the interaction is mainly the ground vibrational state associated with the  $\tilde{B}^2 E'$  electronic state, the extent of mixing being only 0.58%, provided that the spin-orbit constant  $A_{SO}$  is assumed to be 30 cm<sup>-1</sup>. When we adopt assignment II,  $v_3 + v_4$  assigned to 1492 cm<sup>-1</sup>, we may employ a more or less similar procedure, except for the vibrational states interacting with the upper state of the band.

The vibronic Hamiltonian of ref 11 was extended to include the contribution of the  $v_4$  mode, i.e.,  $\mathbf{H'} = \mathbf{H}_{1-3} + \mathbf{H}_{1-4} + \mathbf{H}_{1-4}$  $\mathbf{H}_{2-33} + \mathbf{H}_{2-44} + \mathbf{H}_{2-34}$ , where the first two represent the first-order terms linear in the normal coordinates  $q_3$  and  $q_4$ , respectively, and the last three the second-order terms proportional to  $q_3^2$ ,  $q_4^2$ , and  $q_3q_4$ , respectively. The  $\nu_3$  state in  $\tilde{X}$  will vibronically interact with the  $\tilde{B}$  state  $(\nu_3', \nu_4') =$  $(0,0), (2,0) [\mathbf{H}_{1-3}], (1,1) [\mathbf{H}_{1-4}], (3,0) [\mathbf{H}_{2-33}], (1,2) [\mathbf{H}_{2-44}],$ and (0,1), (2,1) [**H**<sub>2-34</sub>], whereas the  $\nu_3 + \nu_4$  state in X with  $(0,1), (2,1) [\mathbf{H}_{1-3}], (1,0), (1,2) [\mathbf{H}_{1-4}], (3,1) [\mathbf{H}_{2-33}], (1,3)$  $[\mathbf{H}_{2-44}]$ , and (0,0), (2,0), (0,2), (2,2)  $[\mathbf{H}_{2-34}]$ , where the Hamiltonian in square brackets yields the matrix elements. We should perhaps take into account the Franck-Condon type overlap integral and should also pay attention to the different nature of the  $v_3$  mode in the two assignments. Unfortunately, little has been known on the vibrational states in the  $\tilde{B}^2E'$ . We thus concluded that it is still quite difficult at the present to put the argument on a quantitative basis and to compare the extent of mixing of the vibrational states of the  $\tilde{B}^2 E'$  with the  $\nu_3$  state for assignment I and with the  $\nu_3$ +  $\nu_4$  state for assignment II.

Hirota et al.<sup>11</sup> tried to explain why the first-order Coriolis coupling constant of the 1492 cm<sup>-1</sup> band is observed to be much smaller than the force-field value, in terms of the

average angular momentum induced by the degenerate vibrational mode,  $v_3$ . However, they had to assume a quite large value 2440 cm<sup>-1</sup> for the second-order vibronic matrix element. This finding indicates that the mechanism they proposed is by no means a dominant one. On the other hand, Kawaguchi et al.<sup>10</sup> examined the effect of anharmonicity resonance between  $v_3$  and  $v_1 + v_4$  on the first-order Coriolis coupling constant; they transferred necessary molecular parameters from the data on a molecule BF<sub>3</sub> closely resembling the structure of NO<sub>3</sub>. Because of a famous sum rule for the Coriolis coupling constants of the two degenerate normal modes of a planar  $D_{3h}$  XY<sub>3</sub> molecule<sup>28</sup>

$$\zeta_3 + \zeta_4 = 0 \tag{12}$$

the effective value of the Coriolis coupling constant in the  $\nu_3$  state reduces to

$$\zeta_{\rm eff} = (\delta E) \zeta_3 / 2r \tag{13}$$

where  $\delta E$  denotes the unperturbed energy difference between the  $\nu_3$  and  $\nu_1 + \nu_4$  states, i.e., the difference not affected by the anharmonic resonance, whereas

$$2r = \left[ (\delta E)^2 + 4W^2 \right]^{1/2} \tag{14}$$

stands for the perturbed difference. The anharmonic resonance is induced by the cubic anharmonic  $k_{134}$  term, which gives the interaction matrix element *W*:

$$W = k_{134} / 8^{1/2} \tag{15}$$

Kawaguchi et al. thus arrived at a value of  $\zeta_{eff} = 0.568$ , which is still much larger than the observed value. It should, however, be pointed out that, if we increase the BF<sub>3</sub> value of  $k_{134} = 67$ to 107 cm<sup>-1</sup>, we may reproduce the observed data. This  $k_{134}$ value may look too large, but the vibronic interaction is likely to substantially affect the  $v_4$  vibration, in particular, and such an increase of  $k_{134}$  is highly probable. On the other hand, assignment II ascribes the 1492 cm<sup>-1</sup> band to a "pure"  $\nu_3 + \nu_4$ state, in which  $\zeta_3 + \zeta_4 = 0.0$  is expected, while the observed value was  $\xi_3 + \xi_4 = -0.2$ . Although it is still not easy to explain the difference between the observed and calculated  $\zeta_3 + \zeta_4$ values in terms of anharmonicity resonance, because no appropriate candidates for the interacting states are found near the  $\nu_3 + \nu_4$  state, the discrepancy is smaller than that in the case of assignment I, and some additional mechanisms such as that discussed by Hirota et al.<sup>11</sup> (partial quenching of vibrational angular momentum by vibronic interaction) may explain this discrepancy.

As stated above, assignment II ascribes the upper state of the 1492 cm<sup>-1</sup> band to the e' substate of  $v_3 + v_4$ , for which the vibrational angular momentum quantum number  $l = \pm 2$ . Therefore, we expect that the rotational structure, in particular of K' = 1 leading to *l*-type doubling, will differ considerably from that of the fundamental band for which  $l = \pm 1$ , as is, in fact, the case for a molecule closely related to NO<sub>3</sub>, i.e., SO<sub>3</sub> studied in detail by Maki et al.<sup>29</sup> Following Maki we have performed the analysis based on assignment II and have achieved fitting as good as for assignment I, although we introduced more parameters for additional interactions such as those among the e' substate and the other two substates. As is expected, the main *l*-type doubling parameter  $p_{34}$  was found to take a value almost equal to q in assignment I. We are planning to continue studying *l*-type doubling and other related phenomena, which will play crucial roles in clarifying the vibrational assignment.

The molecular constants of <sup>15</sup>NO<sub>3</sub> obtained in the present study will be of great use in future for establishing the vibrational assignment for NO<sub>3</sub> in the ground electronic state, although at present lack of some important information makes it for us unpractical to analyze the isotopic data. One important example of such data is those on the  $v_4$  degenerate mode in the gas phase. These data are indispensable to clarify the details of the vibronic and vibration—rotation interactions and to solve most important pending problems in NO<sub>3</sub>, including the assignment of the 1492 cm<sup>-1</sup> band as one of the most central themes.

# 5. Conclusion

The present study reports the observation and analysis of a few vibration—rotation bands of <sup>15</sup>NO<sub>3</sub> in the gas phase using high-resolution Fourier transform infrared spectroscopy. The results thus obtained are combined with those on <sup>14</sup>NO<sub>3</sub> and others to critically examine the vibrational assignment of NO<sub>3</sub> in the ground electronic state. We demonstrate, on the basis of our gas-phase data, that both assignments I and II involve some problems to be clarified further. To solve these important problems, we need detailed and precise data on NO<sub>3</sub>, including the  $v_4$  fundamental band in the ground electronic state and the observation and analysis of rovibronic transitions among the X, A, and B states.

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**Supporting Information Available:** Tables list all the transition frequencies observed for the 2004, 2128, and 2492  $\text{cm}^{-1}$  bands. This material is available free of charge via the Internet at http://pubs.acs.org.

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