



## The microwave spectrum of the NF radical in the second electronically excited (b 1 $\Sigma$ + ) state: Potentials of three low-lying states (X 3 $\Sigma$ – ,a 1 $\Delta$ ,b 1 $\Sigma$ + )

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# The microwave spectrum of the NF radical in the second electronically excited $(b \, {}^{1}\Sigma^{+})$ state: Potentials of three low-lying states $(X \, {}^{3}\Sigma^{-}, a \, {}^{1}\Delta, b \, {}^{1}\Sigma^{+})$

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The pure rotational transition of the NF radical in the second electronically excited state,  $b^{-1}\Sigma^+$ , was detected by microwave spectroscopy. The NF radical was generated by dc-discharge through a mixture of NF<sub>3</sub> and H<sub>2</sub> at around 90 K. Six rotational transitions for v = 0 and four for v = 1 were observed in the 73–442 GHz region. In addition to the rotational and centrifugal distortion constants, the quadrupole coupling constant of the nitrogen nucleus of NF( $b^{-1}\Sigma^+$ ) was determined for the first time from the lowest two transitions of NF in the v = 0 level. The spectrum of NF( $a^{-1}\Delta$ ) in the first vibrational excited state was also observed in order to derive highly accurate potential parameters for comparison with the data of NF( $X^{-3}\Sigma^-$ ,  $b^{-1}\Sigma^+$ ). © 1998 American Institute of Physics. [S0021-9606(98)01216-1]

#### INTRODUCTION

There are few microwave spectroscopic results on any molecule in the electronically excited states. A small number of molecules have been studied by microwave spectroscopy in the first electronically excited state:  $SO(a \ ^1\Delta)$ ,<sup>1</sup>  $O_2(a \ ^1\Delta_g)$ ,<sup>2</sup>  $CO(a \ ^3\Pi)$ ,<sup>3</sup>  $NF(a \ ^1\Delta)$ ,<sup>4</sup>  $NCl(a \ ^1\Delta)$ ,<sup>5</sup> and  $MgO(a \ ^3\Pi)$ .<sup>6</sup> To date only  $CO(a' \ ^3\Sigma^+)$ ,<sup>7</sup>  $SO(b \ ^1\Sigma^+)$ ,<sup>8</sup> and  $NCl(b \ ^1\Sigma^+)$ <sup>9</sup> have been identified in the second electronically excited state. Although microwave spectroscopy is a powerful tool to characterize molecules in a specific state, only a small number of these studies were carried out because of poor production or fast quenching to the ground state. However, the microwave spectroscopy of metastable molecules which have the advantage of a long radiative lifetime in the electronically excited states is still a challenging area.

The infrared (IR) spectrum of NF in an Ar matrix was observed at 4 K by Milligan and Jacox.<sup>10</sup> The  $b^{-1}\Sigma^+ - X^{-3}\Sigma^-$  and  $a^{-1}\Delta - X^{-3}\Sigma^-$  transitions of the NF radical generated by microwave discharge through NF3 and Ar were subsequently detected<sup>11,12</sup> in the gas phase. Excitation energies of both the  $a^{-1}\Delta$  and  $b^{-1}\Sigma^+$  states were determined to be  $T_0 = 11435.16$  and  $T_e = 18877.05$  cm<sup>-1</sup>, respectively. Hyperfine constants of NF( $a^{-1}\Delta$ ) were determined by gas phase electron paramagnetic resonance.<sup>13,14</sup> Thermal reaction of heated N<sub>2</sub>F<sub>4</sub> and the hydrogen atom was used to produce NF( $a^{-1}\Delta$ ). The Stark effect of NF( $a^{-1}\Delta$ ) was also measured, which resulted in the determination of the dipole moment to be 0.37 D. The rotational transition of the NF radical in the v = 0 to v = 2 levels of the  $a^{-1}\Delta$  state was detected by far-infrared laser magnetic resonance (FIR-LMR).<sup>15,16</sup> Some hyperfine interaction constants were also reported in addition to the rotational and centrifugal constants. Application of laser-induced fluorescence led to the determination of the radiative lifetime of NF( $b^{-1}\Sigma^+$ ) to be 22.6 ms.<sup>17</sup> The vibrational frequency and its anharmonicity,  $\omega_e = 1184$  and

 $\omega_e \chi_e = 8.5 \text{ cm}^{-1}$ , of NF( $a^{-1}\Delta$ ), were derived from a vibrational analysis of the NF( $a^{1}\Delta - X^{3}\Sigma^{-}$ ) transition observed with the  $N_2F_4$  and H reaction.<sup>18</sup> The radiative lifetime of NF( $a^{-1}\Delta$ ) was determined to be 5.6 s. Tunable infrared diode laser spectroscopy was applied to the NF radical in the  $a^{1}\Delta$  and  $X^{3}\Sigma^{-1}$  states.<sup>19,20</sup> The (0,0) band of the  $b^{1}\Sigma^{+}-X^{3}\Sigma^{-1}$  transition by Vervloet and Watson was measured in order to determine the ratio of the perpendicular and parallel transition moments using a Fourier-transform spectrometer.<sup>21</sup> The assignments of Douglas and Jones<sup>11</sup> were confirmed and the molecular constants of both states were improved by this study. Information of highly excited Rydberg states was obtained by recent resonance enhanced multiphoton ionization (REMPI) studies.<sup>22,23</sup> Reaction of an azide radical and a halogen atom is also an efficient reaction to produce a metastable nitrogen halide radical. Several ab initio molecular orbital calculations were conducted on the related low-lying states.24-28

The NF radical is isoelectronic to O<sub>2</sub>. The highest occupied molecular orbital has  $\pi^*$  character, which gives rise to the  $X^{3}\Sigma^{-}$ ,  $a^{1}\Delta$ ,  $b^{1}\Sigma^{+}$  states by the different spin configurations. Electronic transitions from  $a^{-1}\Delta$  or  $b^{-1}\Sigma^+$  states to the  $X^{3}\Sigma^{-}$  are spin forbidden. Therefore, molecules in these metastable states have a relatively long radiative lifetime and are considered to be good candidates for microwave spectroscopy. Our recent microwave spectroscopic result on  $NCl(b^{-1}\Sigma^{+})^{9}$  showed that the potential shape of these lowlying states was similar to SO, which is isovalent to NF and O<sub>2</sub>. The NF radical is expected to show the same similarity. Moreover,  $O_2(a^{-1}\Delta_e) (T_e = 7918.1 \text{ cm}^{-1})^{29}$  can pump the atomic iodine to maintain pulsed lasing on the I\* $\rightarrow$ I transition in the chemical laser system. NCl( $a^{-1}\Delta$ ), in place of  $O_2(a^{-1}\Delta_a)$ , can be used in a similar laser and NF( $a^{-1}\Delta$ ), which has even higher transition energy, is also expected to work.<sup>30</sup> The prospects of a visible laser that operates using the NF( $b^{1}\Sigma^{+}-X^{3}\Sigma^{-}$ ) transition were also examined by Herbelin.<sup>31</sup> Quenching constants of the metastable states

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 $a^{-1}\Delta^{32-36}$  and  $b^{-1}\Sigma^{+18,37-41}$  were extensively studied by Setser and his collaborators from these viewpoints. Du and Setser<sup>40</sup> reported that NF in the  $b^{-1}\Sigma^{+}$  state is efficiently produced by a low power dc discharge in a dilute flow of NF<sub>2</sub> in an Ar carrier.

The pure rotational spectra of NF( $b^{1}\Sigma^{+}$ ) in the v=0and v=1 states and NF( $a^{1}\Delta$ ) in the v=1 state were observed by microwave spectroscopy and their precise molecular constants were determined. Equilibrium structures and potential parameters of the three low-lying states  $(X^{3}\Sigma^{-}, a^{1}\Delta, b^{1}\Sigma^{+})$  are presented. This study is sequential to the previous study on NCl( $b^{1}\Sigma^{+})^{9}$  to experimentally ascertain the similarity between the potentials of low-lying states of NF.

#### EXPERIMENT

A dc-discharge through NF3 and H2 was used to observe microwave spectra of NF( $a^{-1}\Delta$ ) in the ground vibrational state<sup>4</sup> because the reaction of NF<sub>2</sub> with H is a well known reaction to efficiently produce NF in the  $a^{-1}\Delta$  state.<sup>18</sup> The experimental conditions were slightly modified to optimize the production of NF( $a^{1}\Delta$ ) at 90 K. This modification caused the intensity of NF( $a^{-1}\Delta$ ) to be much stronger than with the previous conditions at around 190 K. The transition frequencies of NF( $b^{1}\Sigma^{+}$ ) were calculated based on the emission study.<sup>21</sup> A series of diamagnetic lines was found near the predicted frequencies. These transitions disappeared as soon as either the flow of the chemicals was cut off or the discharge was stopped. The assignment was confirmed by the fact that splittings due to N were observed in the low-J transitions. The transitions in the v=1 state were predicted by using the results of emission spectroscopy.<sup>11</sup> A series of transitions showing similar dependency on the composition of chemicals and the discharge current was assigned to be the vibrational excited state of NF( $b^{1}\Sigma^{+}$ ). Intensity of this higher state was about a tenth of that of the ground vibrational state. All the spectral lines were measured by a spectrometer combined with a 2-m free-space cell at the Institute for Molecular Science.<sup>42</sup> Measurements were carried out by cooling the cell down to around 90 K with liquid nitrogen. The optimized condition at around 90 K was a dc discharge (10 mA) through a mixture of  $NF_3(16 \text{ mTorr})$  and  $H_2(18 \text{ mTorr})$ . This production system gave strong signals of NF( $a^{-1}\Delta$ ) with a factor of 10 or more greater intensity than with the previous condition.<sup>4</sup> The background pressure was 1-2 mTorr. For the ground vibrational state, six rotational transitions from N=1-0 to 6-5 were measured in the 73-442 GHz region, and for the vibrational excited state, four transitions from N=3-2 to 6-5 were observed. Figure 1 shows the N=2-1 transition which splits into two lines by the N nuclear quadrupole interaction. The observed spectral lines of NF( $b^{1}\Sigma^{+}$ ) in the v=0 and v=1 states are listed in Table I.

The transition frequencies of NF( $a^{-1}\Delta$ ) in the v=1 state were calculated based on the constants given by far-infrared LMR.<sup>16</sup> A similar pattern to the ground vibrational state was found near the predicted frequencies. These measurements were carried out under the same condition as NF( $b^{-1}\Sigma^+$ ). Nineteen hyperfine components of three rotational transitions



FIG. 1. The N=2-1 transition in the v=0 state of NF( $b^{-1}\Sigma^+$ ). The splitting is due to the nuclear quadrupole interaction of the nitrogen nucleus. The NF was generated by a dc discharge through a mixture of NF<sub>3</sub> and H<sub>2</sub> at a total pressure of 35 mTorr. The integration time was 40 s.

from J=3-2 to 5-4 were observed in the 217-362 GHz region. The intensity ratio of the v=1 state to the v=0 state for both NF( $a^{-1}\Delta, b^{-1}\Sigma^{+}$ ) was about 0.1 for the J=5-4transition, however, this ratio depended strongly on the discharge current. The experimental transition frequencies of NF( $a^{-1}\Delta$ ) in the v=1 state are listed in Table II. Transitions due to NF( $a^{-1}\Delta$ ) in the v=2 state were also identified, but

TABLE I. Observed rotational transitions of NF( $b^{-1}\Sigma^+$ ).

N'-N	F'-F	$\nu_{\rm obs}~({\rm MHz})^{\rm a}$	$\Delta \nu$ (obscalc.) (MHz)
		v = 0	
1 - 0	2 - 1	73 773.085(26)	0.010
1 - 0	1 - 1	73 774.376(23)	0.021
2 - 1	3-2	14 7542.700(8)	-0.023
2 - 1	2 - 1		
2 - 1	1 - 0	14 7543.922(37)	-0.019
2 - 1	2 - 2		
3-2	4-3	22 1304.720(7)	0.006
3-2	3-2		
3-2	2 - 1		
4-3	5-4	295 055.253(2)	0.023
4-3	4-3		
4-3	3-2		
5-4	6–5	368 790.570(8)	-0.013
5-4	5-4		
5-4	4-3		
6–5	7-6	442 506.974(8)	0.001
6–5	6–5		
6–5	5-4		
		v = 1	
3-2	4-3	218 688.689(11)	0.003
3-2	3-2		
3-2	2 - 1		
4-3	5-4	291 567.305(22)	0.002
4-3	4-3		
4-3	3-2		
5 - 4	6-5	364 430.843(6)	-0.008
5 - 4	5-4		
5-4	4-3		
6-5	7–6	437 275.559(19)	0.004
6-5	6-5		
6-5	5-4		

<sup>a</sup>The numbers in parentheses represent the variances of the observed value in units of the last significant digits.

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TABLE II. Observed rotational transitions of NF( $a^{-1}\Delta$ ) in the v=1 state.

J'-J	$F_1 - F_1$	F'-F	$\nu_{\rm obs}~({\rm MHz})^{\rm a}$	$\Delta \nu$ (obs-calc) (MHz)
3-2	3.5-2.5	4.5-3.5	217 142.181(4)	0.012
3-2	3.5-2.5	3.5 - 2.5	217 205.550(3)	-0.015
3-2	3.5-2.5	2.5 - 1.5	217 241.328(6)	-0.018
3-2	2.5 - 1.5	3.5 - 2.5	217 529.221(3)	-0.015
3-2	2.5 - 1.5	2.5 - 1.5	217 602.690(7)	-0.010
3-2	2.5 - 1.5	1.5 - 0.5	217 626.948(15)	0.013
4-3	4.5-3.5	5.5 - 4.5	289 624.031(8)	0.015
4-3	4.5-3.5	3.5 - 2.5	289 679.430(8)	0.006
4-3	3.5 - 2.5	4.5-3.5	289 826.642(9)	-0.008
4-3	3.5 - 2.5	3.5 - 2.5	289 863.792(8)	0.022
4-3	3.5-2.5	2.5 - 1.5	289 881.968(7)	0.008
5 - 4	5.5 - 4.5	6.5 - 5.5	362 058.174(40)	0.016
5 - 4	5.5 - 4.5	5.5 - 4.5	362 079.129(10)	-0.007
5 - 4	5.5 - 4.5	4.5-3.5	362 093.518(10)	-0.009
5 - 4	4.5-3.5	5.5 - 4.5	362 183.772(6)	0.005
5 - 4	4.5-3.5	4.5-3.5	362 206.094(8)	0.019
5 - 4	4.5-3.5	3.5 - 2.5	362 219.159(9)	-0.022
5 - 4	5.5 - 4.5	4.5 - 4.5	362 004.679(11)	-0.004
5-4	4.5-3.5	3.5-3.5	362 133.053(5)	-0.015

<sup>a</sup>The numbers in parentheses represent the variances of the observed value in units of the last significant digits.

not measured precisely in the present study. Preliminary results showed that the intensity ratio to the v = 1 state is much larger than 0.1.

#### ANALYSIS

The conventional Hamiltonian appropriate for the  ${}^{1}\Sigma^{+}$  state was used to analyze the spectra of the NF( $b^{-1}\Sigma^{+}$ ) state. The nuclear quadrupole interaction of the nitrogen nucleus is also considered. The same coupling scheme, a sequential addition of the angular momenta as  $F_1=J+I_F$  and  $F=F_1$  $+I_N$ , and the same matrix elements as NF( $a^{-1}\Delta$ ) in the v = 0 state,<sup>4</sup> were used to calculate the transition frequencies of NF( $a^{-1}\Delta$ ) in the v=1 state. Molecular constants obtained by the least-squares method of eight and four transitions of NF( $b^{-1}\Sigma^{+}$ ) in the ground vibrational state and the first vibrational excited state, respectively, are listed in Table III. In Table IV, molecular constants of NF( $a^{-1}\Delta$ ) in the v=1 state are given. The standard deviations of the fit of NF( $b^{-1}\Sigma^{+}$ ) in the v=1 transitions were 21 and 7 kHz, re-

TABLE IV. Molecular constants of NF( $a^{-1}\Delta$ ) (MHz).<sup>a</sup>

	MW		Far-infrared LMR <sup>b</sup>	
υ	0 <sup>c</sup>	1	0	1
B	36 653.5816(33)	36 218.8882(47)	36 653.82(150)	36 218.53(150)
D	0.159 102(88)	0.157 809(129)	0.1589(60)	0.1559(45)
$a(\mathbf{F})$	758.960(27)	748.37(20)	758.1(3)	717(3)
a(N)	110.019(17)	110.172(37)	109.7(15)	107(1.5)
eQq(N)	4.177(81)	4.317(97)	4.1(15)	4(1.5)
$C_{I}(F)$	0.0991(75)	0.082(51)		
$C_{I}(N)$	0.0135(63)	0.0135 <sup>d</sup>		
rms	0.014	0.016		

<sup>a</sup>The numbers in parentheses represent three standard deviations in units of the last significant digits. <sup>b</sup>Ref. 16.

<sup>c</sup>Ref. 4. <sup>d</sup>Fixed.

TABLE III. Molecular constants of NF( $b^{-1}\Sigma^+$ ) (MHz).<sup>a</sup>

	MW		Emission	
υ	0	1	0 <sup>b</sup>	1°
В	36 886.9601(82)	36 450.9376(33)	36 886.9(38)	36454
D	0.158 045(151)	0.157 058(59)	0.1584(74)	0.158
eQq(N)	4.267(185)	4.267 <sup>d</sup>		
rms	0.021	0.007		

<sup>a</sup>The numbers in parentheses represent three standard deviations in units of the last significant digits.

<sup>b</sup>Ref. 21.

<sup>c</sup>Ref. 11. <sup>d</sup>Fixed.

spectively, and that of NF( $a^{-1}\Delta$ ) in the v = 1 state was 16 kHz. These deviations are satisfactory compared with frequency measurement errors, as shown in Tables I and II. Equilibrium molecular constants of NF( $b^{-1}\Sigma^+$ ) and NF( $a^{-1}\Delta$ ) are shown in Tables V and VI, respectively. The equilibrium a(F), a(N), and eQq(N) were also calculated by an expansion similar to the rotational term and shown in Table VI, i.e.,

$$X_{\nu} = X_{e} + \alpha^{X}(\nu + 1/2) + \beta^{X}(\nu + 1/2)^{2} + \cdots$$
 (1)

The preliminary data of NF( $a^{-1}\Delta$ ) in v=2 were not used in the derivation of equilibrium molecular constants.

### DISCUSSION

The molecular constants of NF( $b^{-1}\Sigma^{+}$ ) determined in the present study are in good agreement with previous emission studies. The eQq(N) was found to be the same as that of NF( $a^{-1}\Delta$ ) within experimental uncertainties. This result was as expected from the fact that the eQq(Cl) constants of NCl in the  $a^{-1}\Delta$  and  $b^{-1}\Sigma^{+}$  are also almost the same. The vibrational frequency calculated by  $D_e = 4B_e^{-3}/\omega_e^2$  was consistent with the result of the emission spectrum.<sup>11</sup>

Rotational and centrifugal distortion constants of NF( $a^{1}\Delta$ ) in the v = 1 state are consistent with the previous FIR-LMR study. According to the LMR result<sup>16</sup> of NF( $a^{1}\Delta$ ), there is a significant decrease in a(F) in passing

TABLE V. Equilibrium parameters of NF( $b^{-1}\Sigma^+$ ).<sup>a</sup>

	This study	Emission <sup>b</sup>
$B_e$ (MHz)	37 104.9714(124)	37105
$D_e$ (MHz)	0.158 54(23)	0.158
$\alpha_e$ (MHz)	436.0225(88)	434.1
$\beta_e$ (MHz)	-0.000987(162)	
$\omega_e (\mathrm{cm}^{-1})^{\mathrm{c}}$	1197.54(86) <sup>c</sup>	1197.49

<sup>a</sup>The numbers in parentheses represent three standard deviations in units of the last significant digits.

from v = 0 to v = 1 while a(N) remains almost constant. Our

<sup>b</sup>Ref. 11.

<sup>c</sup>Derived by the following relation,  $D_e = 4B_e^3 / \omega_e^2$ .

TABLE VI. Equilibrium parameters of NF( $a^{-1}\Delta$ ).<sup>a</sup>

	This study	Other results
$B_e$ (MHz)	36 870.9283(55)	36 871.5(24) <sup>b</sup>
$D_e$ (MHz)	0.159 749(147)	0.1604(93) <sup>b</sup>
$\alpha_e$ (MHz)	434.6934(57)	435.3(21) <sup>b</sup>
$\beta_e$ (MHz)	-0.001 293(156)	$-0.0030(75)^{b}$
a(F) (MHz)	764.255(108)	
a(N) (MHz)	109.943(32)	
eQq(N) (MHz)	4.037(131)	
$\omega_e \ (\mathrm{cm}^{-1})$	1181.73(54) <sup>c</sup>	1182.95 <sup>d</sup>

<sup>a</sup>The numbers in parentheses represent three standard deviations in units of the last significant digits.

of NF(X  ${}^{3}\Sigma^{-}$ ) might be due to the underestimation of

<sup>b</sup>Converted from the value in Table V of Ref. 16.

<sup>c</sup>Derived by the following relation,  $D_e = 4B_e^3/\omega_e^2$ .

<sup>d</sup>Ref. 18.

result, however, did not show such a critical change as that of the LMR result. Preliminary experiment of NF( $a^{-1}\Delta$ ) in the v=2 state showed that a(F) is about 738 MHz, that is, a(F) decreases by about 10 MHz by going up one vibrational level. This gradual decrease means a decrease in electron orbital spin density at the fluorine nucleus.

The rotational part of the internuclear potential may be written in the following form when Dunham expansion<sup>43</sup> is utilized,

$$U = a_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + \cdots), \tag{2}$$

where,

į

$$\xi = \frac{r - r_e}{r_e}.$$
(3)

The Dunham expansion coefficients are related to the conventional rotational constants since  $B_e^2/\omega_e^2$  is of the order of  $10^{-6}$ . Assuming  $Y_{11}$  and  $Y_{12}$  to be  $-\alpha_e$  and  $-\beta_e$ , cubic and quartic internuclear potential constants,  $a_1$  and  $a_2$ , were determined for NF( $a^{-1}\Delta, b^{-1}\Sigma^+$ ). In the case of NF( $X^{-3}\Sigma^-$ ), as no microwave data or significant datum of  $\beta_e$  are available,  $\omega_e \chi_e$  was used instead to estimate  $a_2$ . The potential parameters and equilibrium molecular constants of three low-lying states of NF and NCl are tabulated in Table VII. It is to be noted that smaller errors of the potential parameters

TABLE VII. Potential constants of NF and NCl.<sup>a</sup>

the errors of $\omega_e$ and $\omega_e \chi_e$ . Negative $\beta_e$ of
NF( $X^{3}\Sigma^{-}, a^{1}\Delta, b^{1}\Sigma^{+}$ ) indicates that the ratio of $a_{2}$ to $a_{1}$
is relatively large and that Morse potential is not a very good
approximation as it is for NCl. <sup>9</sup> The depth of the internuclear
potential is governed by $a_0$ and the deviations from har-
monic potential are governed by $a_1$ and $a_2$ . The similarity of
$a_1$ and $a_2$ near the equilibrium geometry shows that the
shapes of the potentials of the low-lying states resemble each
other but the change of spin orientation decreases the total
other but the change of spin offentation decreases the total
energy of NF from the b to X states, while it decreases the
bond strength $(\omega_e)$ of NF. This is the same for NCl. The
equilibrium bond lengths, $r_e$ , are also tabulated in Table VII,
where the three standard errors in Planck's constant and the
atomic mass unit <sup>44</sup> are included in error estimation. This er-
ror should be underestimated because NF( $a^{-1}\Delta$ ) in $v=2$
shows the necessity of inclusion of higher order vibration-
rotation constant ( $\gamma$ ) which affects the equilibrium rota-
tional constant on the order of several MHz. The $a_1$ , $r_2$ and
tional constant on the order of several wire. The $u_0, r_e$ , and
$\omega_e$ constants are closely related and the decrease in $r_e$ and
the increase in $a_0$ and $\omega_e$ from the X ${}^{3}\Sigma^{-}$ state to the $b^{-1}\Sigma^{+}$

Several production methods using dc-discharge were at-

state is again the same as observed for NCl.

TABLE VII. FOR	intial constants of NF and NCI.		
	$NF(X^{3}\Sigma^{-})$	$NF(a^{-1}\Delta)$	$NF(b^{-1}\Sigma^+)$
$\omega_e \ (\mathrm{cm}^{-1})$	1141.37 <sup>b</sup>	1181.73(54) <sup>c</sup>	1197.54(86) <sup>c</sup>
$a_0 ({\rm cm}^{-1})$	270 123(36)	283 864(261)	289 673(417)
<i>a</i> <sub>1</sub>	-2.948(21)	$-2.888\ 00(87)$	-2.894 98(136)
$a_2$	5.895(154)	5.908(78)	5.792(83)
$r_e$ (Å)	1.316 979(88)	1.303 956 31(166)	1.299 837 39(166)
	$NCl(X^{3}\Sigma^{-})$	$NCl(a^{-1}\Delta)^d$	$\mathrm{NCl}(b^{-1}\Sigma^+)^{\mathrm{d}}$
$\omega_e (\mathrm{cm}^{-1})$	827.9578(26) <sup>e</sup>	905.498(187) <sup>c</sup>	936.75(99) <sup>c</sup>
$a_0 ({\rm cm}^{-1})$	$263\ 723.88(162)^{d}$	302 859(125)	319 922(676)
<i>a</i> <sub>1</sub>	$-3.09602(23)^{d}$	-3.073 37(43)	-3.0995(22)
<i>a</i> <sub>2</sub>	$6.5442(27)^{d}$	6.612(49)	6.392(176)
$r_e$ (Å)	1.610 705(19) <sup>e</sup>	1.578 272 6(20)	1.568 006 9(20)

<sup>a</sup>The numbers in parentheses represent three standard deviations in units of the last significant digits. <sup>b</sup>Ref. 11.

<sup>c</sup>Derived by the following relation,  $D_e = 4B_e^3/\omega_e^2$ . <sup>d</sup>Ref. 9. <sup>e</sup>Ref. 46.

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tempted to observe NF( $b^{1}\Sigma^{+}$ ). The following gaseous combinations, (1) NF<sub>3</sub> and H<sub>2</sub>, (2) NF<sub>3</sub>, H<sub>2</sub>, and He, (3) N<sub>2</sub> and  $F_2(5\%$  diluted in He), (4) NF<sub>3</sub> and Ar at a temperature of around 200 K, were not successful. The optimum condition of NF( $b^{1}\Sigma^{+}$ ) was obtained by optimizing the production efficiency of NF( $a^{-1}\Delta$ ). The low temperature and discharge current condition made the signal of NF( $a^{-1}\Delta$ ) about ten times stronger, as mentioned in the Experiment section. Molecules, whose second excited electronic states have been studied so far by microwave spectroscopy, were generally produced by discharge at the current of several hundred mA. The low discharge current used in this experiment looks somewhat irregular,<sup>40</sup> however, NF( $b^{-1}\Sigma^+$ ) is also produced by the energy transfer reaction of NF( $a^{-1}\Delta$ ) and HF( $v \ge 2$ ) when in the case of the azide radical and the fluorine atom reaction.<sup>32</sup> It may be supported by the fact that the addition of He or Ar gas at around 90 K did not increase the signal even though metastable He is often responsible in exciting molecules in the ground electronic states. In this study, the ratio of production of NF( $a^{-1}\Delta$ ) to that of NF( $b^{-1}\Sigma^+$ ) in the ground vibrational state was 170:1 by assuming no difference between the dipole moments of both states. As NF( $b^{-1}\Sigma^+$ ) is expected to possess a larger dipole moment,<sup>27</sup> this ratio may even decrease.

The NF( $X^{3}\Sigma^{-}$ ) radical was not observed in the course of this study. This is unusual, as the ground state species are usually more abundant than the metastable state in the discharge cell. If this also applies to the NF radical under the experimental condition in our system, then at least the same amount of NF(X  ${}^{3}\Sigma^{-}$ ) ought to be produced as that of NF( $a^{-1}\Delta$ ). This results in the dipole moment of NF( $X^{-3}\Sigma^{-1}$ ) as estimated to be less than 0.02 D, which is reasonable when compared with the predicted value of  $-0.0327^{27}$  or  $-0.081 \text{ D}^{25}$  from *ab initio* molecular orbital (MO) studies. However, there is still the possibility that NF(X  ${}^{3}\Sigma^{-}$ ) is readily removed in this experimental system. Several reactions of NF(X  ${}^{3}\Sigma^{-}$ ) have been considered as a potential removal scheme.<sup>45</sup> The inference is that the reaction of  $NF(X^{3}\Sigma^{-})$  with NF<sub>2</sub> may well be the dominant removal mechanism and provide an explanation to our failure, although the differing conditions in both studies prevent a conclusive proof.

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