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Kaori Kobayashi, Masahiro Goto, Satoshi Yamamoto, and Shuji Saito

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The microwave spectrum of the NCI radical in the electronically excited ($a^{1}\Delta$) state

Kaori Kobayashi and Masahiro Goto^{a)} Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444, Japan

Satoshi Yamamoto

Department of Physics, School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

Shuji Saito

Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444, Japan

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The pure rotational spectrum of the ¹⁴N³⁵Cl radical in the first electronically excited a ¹ Δ state was detected by microwave spectroscopy. The NCl radical was produced by a dc-glow discharge of an N₂ and Cl₂ mixture between 175–210 K. Seven rotational transitions for v=0 and five for v=1, showing hyperfine structures due to the nitrogen and chlorine nuclei, were observed in the 162–404 GHz region. The rotational, centrifugal distortion, and hyperfine coupling constants including nuclear spin–rotation coupling constant of the chlorine nucleus were determined accurately by a least-squares analysis of the measured frequencies. The equilibrium structural parameters were derived and discussed. © 1996 American Institute of Physics. [S0021-9606(96)02222-2]

INTRODUCTION

The reports on microwave spectra of the electronically excited states have been rather limited since its first report on the SO($a^{-1}\Delta$) radical in 1970.¹ One of the reasons is a difficulty in producing electronically excited molecules efficient enough to be detected by microwave spectroscopic method. So far studies on $O_2(a \ {}^1\Delta_{\rho})$, $^2 CO(a \ {}^3\Pi, b \ {}^3\Sigma^+)$, $^{3,4} NF(a \ {}^1\Delta)$, 5 and SO($b^{-1}\Sigma^+$) (Ref. 6) molecules were reported in addition to the 1970 report on SO($a^{-1}\Delta$). Generally, electronic transitions between the states studied and the ground electronic states are strongly forbidden by spin and/or orbital angular momentum conservation rules, that is, the states studied are metastable states. The excitation energy of the above metastable states ranges from 0.8 to 7 eV.⁷ The delta singlet oxygen is efficiently generated in discharged plasma of oxygen, CO is easily excited to the $a^{3}\Pi$ or $b^{3}\Sigma^{+}$ state by the energyexchange reaction of CO with the excited helium atom, NF(a) $^{1}\Delta$) is produced by exothermic reaction of the hydrogen atom with the NF₂ radical, and SO is excited into the $a^{-1}\Delta$ or $b^{-1}\Sigma$ state by a spin-exchange reaction of SO(X ${}^{3}\Sigma^{-}$) with O₂(a $^{1}\Delta_{a}$). The detailed molecular constants of electronically excited states make clear how the molecular structure changes by an electronic excitation in the molecule. The changes in the molecular constants could give us clues to understanding changes in chemical reactivity of the molecules in the ground electronic state and the electronically excited state.

The NCl radical, similar to the NF radical, has the first electronically excited state at about 1 eV above the ground electronic state, and the electronic transition between the $a^{1}\Delta$ state and the $X^{3}\Sigma^{-}$ state is strongly forbidden. Therefore the NCl radical in the $a^{1}\Delta$ state has a relatively long lifetime and is a good candidate to be studied by microwave spec-

troscopy. The first spectroscopic identification of the NCl radical was made by Milligan⁸ observing the infrared bands of NCl produced by photolysis of ClN₃ trapped in an argon matrix at 4.2 K. The microwave spectrum of NCl in the ${}^{3}\Sigma^{-}$ ground electronic state was studied by Yamada and his collaborators⁹⁻¹¹ using a glow discharge of a nitrogen and chlorine gas mixture. They determined its detailed molecular constants and derived the spin densities of unpaired electrons for nitrogen and chlorine atoms. The electronic spectra of NCl were studied for $A^{3}\Pi - X^{3}\Sigma^{-}$ as well as $b^{1}\Sigma^{+} - X^{3}\Sigma^{-}$ in the sixties, 12,13 but it was in 1980 that the $a^{-1}\Delta$ state of NCl was made clear through observations of emission spectra in the near infrared region.¹⁴ Pritt and his collaborators¹⁵ found that the reaction of the chlorine atom with the molecular azide efficiently generates the NCl radical in the $a^{-1}\Delta$ state as well as the $b^{-1}\Sigma^+$ state, and observed the $a^{-1}\Delta - X$ ${}^{3}\Sigma^{-}$ transition and the $b {}^{1}\Sigma^{+}-X {}^{3}\Sigma^{-}$ transition in emission. They determined the vibrational constants for the $a^{-1}\Delta$ state and T_e to be 9260 cm⁻¹. However, so far no molecular constants related to rotational motion and hyperfine interaction have been available for the $a^{-1}\Delta$ state. Several quantum chemical calculations were made to predict the molecular properties of NCl including its geometrical structure,¹⁶⁻¹⁸ electronic structure,¹⁹ and radiative lifetime.^{20,21}

In the present study, we have observed the pure rotational spectrum of NCl($a^{-1}\Delta$) in the v=0 and v=1 states by microwave spectroscopy, determined its precise molecular constants, and we derived the equilibrium structure.

EXPERIMENT

The spectral lines of NCl in the $a^{-1}\Delta$ state were first detected by using a dc-glow discharge in a mixture of AlCl₃ and N₂ with a millimeter-wave spectrometer at Nagoya University.⁴ The identification of the spectral lines was based

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^{a)}Present address: National Industrial Research Institute of Nagoya, Hiratecho, Kita-ku, Nagoya Aichi 462, Japan.



FIG. 1. The J=9-8 transition in the v=0 state of NCl($a^{-1}\Delta$). The NCl was generated by a dc-glow discharge in a 1:1 mixture of N₂ and Cl₂ (9.98% dispersed in helium gas) at a total pressure of 40 mTorr. The integration time was 20 s.

on production chemistry indicating the necessity of chlorine and nitrogen atoms, and we tentatively derived a rotational constant from the observation of the complicated spectral patterns. Then, all the spectral lines in the millimeter- and submillimeter-wave regions were measured by a spectrometer combined with a 2 m free-space cell at the Institute for Molecular Science.²²

The production of NCl was optimized by monitoring its spectral lines of the ground electronic state.9 The measurements were carried out by cooling the cell to the temperature of 175-210 K with liquid nitrogen. For the precise frequency measurements of the spectral line frequencies, a dc-glow discharge in a 1:1 mixture of N2 and Cl2 (9.98% dispersed in helium gas) was used, because this production system gave a smaller number of disturbing lines due to diamagnetic molecules, and also reasonably strong signals of NCl($a^{-1}\Delta$). A larger discharge current (150 mA) and a higher pressure (40 mTorr) than the condition⁹ of NCl in the ground electronic state were required to obtain sufficient intensity of NCl($a^{-1}\Delta$) in the v=0 state transition. Observed line widths range from 0.5 to 0.7 MHz. The Λ -type doubling splitting was not observed. For the ground vibrational state, we observed seven rotational transitions from J=4-3 to 10-9 in the 162-404 GHz region. Each rotational transition splits into 12 components due to hyperfine interaction of the nitrogen and chlorine nuclei so that in total 70 spectral lines in the v=0 state were measured. The lines with J=4-3 state were so weak that only four components were measured, and with high Jsome components overlapped with each other. Figure 1 shows an example of the whole spectral pattern for the J=9-8 transition. The observed spectral lines in the v=0state are listed in Table I.

The transition frequencies of NCl($a^{1}\Delta$) in the v=1 state were estimated²³ from the anharmonicity constant, χ_e , given by infrared emission spectroscopy.¹⁵ The J=9-8 transition frequency in the v=1 state is thus expected to be lower than that of the ground state by 2.7 GHz. Hence, we have searched for them in the 361 GHz region. Complicated spectral lines similar to the ground vibrational state lines were

TABLE I. Observed rotational transitions of NCl $(a^{-1}\Delta)$ in the $v=0$ state.					
J'-J	G	F'-F	$\nu_{\rm obs}~({\rm MHz})^{\rm a}$	$\Delta \nu$ (obscalc.) (MHz)	Weight
4-3	2.5	6.5-5.5	161 514.573(6)	-0.018	1.0
4-3	2.5	5.5-4.5	161 562.446(19)	-0.257	0.0 ^b
4-3	1.5	5.5-4.5	161 532.878(24)	0.002	1.0
4-3	0.5	4.5-3.5	161 551.625(27)	0.077	0.0
5-4	2.5	1.5-0.5	201 912.416(15)	-0.033	1.0
5-4 5-4	2.5	0.5-5.5 5 5-4 5	201 959.380(20)	-0.004	1.0
5-4	2.5	45 - 35	201 979 138(36)	-0.020	1.0
5-4	2.5	3.5-2.5	201 989.791(41)	-0.023	1.0
5-4	2.5	2.5-1.5	201 994.475(62)	0.019	1.0
5-4	1.5	6.5-5.5	201 924.924(19)	-0.011	1.0
5-4	1.5	5.5 - 4.5	201 946.292(21)	-0.004	1.0
5-4	1.5	4.5-3.5	201 963.951(50)	-0.029	1.0
5 - 4	1.5	3.5 - 2.5	201 974.150(11)	-0.006	1.0
5 - 4	0.5	5.5 - 4.5	201 937.438(15)	0.033	1.0
5 - 4	0.5	4.5-3.5	201 954.479(34)	-0.006	1.0
6–5	2.5	8.5-7.5	242 298.360(15)	0.111	0.0^{bd}
6-5	2.5	7.5-6.5	242 315.429(18)	-0.035	1.0
6–5	2.5	6.5-5.5	242 330.366(7)	0.006	1.0
6-5	2.5	5.5-4.5	242 341.168(29)	-0.187	0.0^{bc}
0-3 6-5	2.5	4.5-5.5	242 349 398(31)	-0.006	1.0
0-5 6-5	2.5	35_25	242 349.398(31)	0.000	1.0
6-5	1.5	7.5-6.5	242,307,352(13)	0.001	1.0
6-5	1.5	6.5-5.5	242 321.078(20)	-0.006	1.0
6-5	1.5	5.5-4.5	242 333.155(18)	0.049	1.0
6-5	0.5	6.5-5.5	242 316.252(16)	0.009	1.0
6-5	0.5	5.5 - 4.5	242 328.002(21)	0.006	1.0
7-6	2.5	9.5 - 8.5	282 674.241(5)	0.039	1.0
7-6	2.5	8.5-7.5	282 686.027(11)	0.018	1.0
7–6 7–6	2.5 0.5	7.5–6.5 6.5–5.5	282 696.512(10)	0.005	1.0 ^c
7-6	2.5	6.5 - 5.5	282 704.580(10)	-0.060	0.0^{b}
7-6	2.5	5.5 - 4.5	282 710.485(18)	0.011	1.0
7–6	2.5	4.5-3.5	282 714.864(12)	0.001	1.0
7–6	1.5	8.5-7.5	282 681.160(12)	0.021	1.0
7-6	1.5	7.5-6.5	282 690.681(20)	0.014	1.0
7-6	1.5	6.5-5.5	282 699.278(9)	0.004	1.0
/-0 7.6	1.5	5.5-4.5 75.65	282 /05.//1(6)	0.035	1.0
7-0 8-7	2.5	10.5 9.5	202 007.703(0)	-0.001	1.0
8-7	2.5	95-85	$323\ 040.097(2)$ $323\ 049\ 289(12)$	0.001	1.0
8-7	2.5	8.5-7.5	323 057.049(6)	-0.029	1.0
8–7	2.5	7.5–6.5	323 063.187(6)	-0.016	1.0
8-7	2.5	6.5-5.5	323 067.710(4)	0.004	1.0
8-7	2.5	5.5 - 4.5	323 071.590(11)	-0.015	1.0
8-7	1.5	9.5-8.5	323 046.158(12)	0.002	1.0
8-7	1.5	8.5-7.5	323 053.129(9)	-0.017	1.0
8-7	1.5	7.5 - 6.5	323 059.505(9)	-0.006	1.0
8-7	1.5	6.5 - 5.5	323 064.958(9)	-0.005	1.0
8-7	0.5	8.5-7.5	323 051.279(9)	-0.023	1.0
8-7	0.5	7.5-6.5	323 058.133(5)	0.016	1.0
9-8	2.5	11.5-10.5	363 397.381(8)	-0.003	1.0
7-8 0 0	2.3 2.5	10.3-9.3	363 403.871(4)	0.003	1.0
2-0 9_8	2.3 2.5	9.5-0.5 8 5-7 5	363 414 688(10)	0.013	1.0
2-0 9_8	2.3 2.5	0.5-7.5 7 5_6 5	363 418 247(12)	-0.001	1.0
9_8	2.5	6.5-5.5	363 421 660(21)	-0.003	1.0
9-8	1.5	10.5-9.5	363 401.778(6)	-0.011	1.0
9-8	1.5	9.5-8.5	363 407.164(5)	0.025	1.0
9-8	1.5	8.5-7.5	262 411 706(12)	0.000	1.00
9-8	0.5	8.5-7.5	303 411./06(13)	0.009	1.0~
9-8	1.5	7.5-6.5	363 416.629(8)	-0.035	1.0
9-8	0.5	9.5-8.5	363 405.856(2)	-0.032	1.0

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TABLE I. (Continued.)

J'-J	G	F'-F	$\nu_{\rm obs}~({\rm MHz})^{\rm a}$	Δu (obscalc.) (MHz)	Weight
10–9	2.5	12.5-11.5	403 743.588(10)	0.001	1.0
10-9	2.5	11.5 - 10.5	403 748.686(5)	0.026	1.0
10-9	2.5	10.5 - 9.5	403 753.441(15)	-0.012	1.0
10-9	2.5	9.5-8.5	403 757.309(8)	0.010	1.0
10-9	2.5	8.5-7.5	102 550 500(12)	0.064	o obc
10-9	1.5	8.5-7.5	403 759.789(13)	0.064	0.050
10-9	2.5	7.5-6.5	403 763.195(4)	0.001	1.0
10-9	1.5	11.5-10.5	403 747.172(16)	-0.038	1.0
10-9	1.5	10.5 - 9.5	402 751 042(11)	0.040	1.00
10-9	0.5	10.5 - 9.5	403 751.043(11)	0.049	1.0°
10-9	1.5	9.5-8.5			
10-9	0.5	9.5-8.5	403 755.193(11)	0.009	1.0°

^aThe numbers in parentheses represent the variances of the observed value in units of the last significant digits.

^bNot included in the fit.

^cOverlap of two NCl spectral lines.

^dNot accurately measured due to the disturbance.

found at about 360 GHz, which is lower than the v=0 line frequency by 3.4 GHz. Then, other lines were found readily. In this way five rotational transitions were observed. This vibrational excited state species was generated by dc-glow discharge (150-300 mA) of N₂ (7 mTorr) and Cl₂ diluted with helium gas (20 mTorr) between 175-210 K. In this temperature range, the intensity does not depend dramatically on the temperature though the optimized temperature was about 195 K. Around 170 K, the lines disappeared which corresponds to the freeze out of chlorine gas (m.p. 172.17 K). While searching the optimum condition for the v=1 state, we noted that cleanliness of the cell affected the production efficiency of the metastable molecules, because the transitions of using NCl($a^{-1}\Delta$) were not observed by using a cell which had been used in the prior experiment using Si compound. We observed five rotational transitions of J=6-5 to 10-9 in v=1 state, 49 components in total. The intensity ratio of the v=1 state to the v=0 state was evaluated to be roughly 0.3 for the J=9-8, G=2.5, and F=11.5-10.5 transition with a discharging current at 300 mA. The vibrational temperature was roughly estimated to be 1100 K from the intensity ratio of two vibrational states, assuming that the dipole moments in both states are the same. The observed transition frequencies for the v=1 state are listed in Table II.

ANALYSIS

In the initial stage of the analysis, we used the coupling scheme of a sequential addition of the angular momenta as $F_1 = J + I_{Cl}$ and $F = F_1 + I_N$, and evaluated the matrix elements of the appropriate Hamiltonian⁵ given as

$$H = H_{\rm rot} + H_{\rm hfs}, \tag{1}$$

where

$$H_{\rm rot} = B[J(J+1) - \Lambda^2] - D[J(J+1) - \Lambda^2]^2, \qquad (2)$$

$$_{\text{rot}} = B[J(J+1) - \Lambda^2] - D[J(J+1) - \Lambda^2]^2, \qquad (2)$$

J'-J	G	F'-F	$\nu_{\rm obs}~({\rm MHz})^{\rm a}$	$\Delta \nu$ (obscalc.) (MHz)	Weight
6–5	2.5	8.5-7.5	240 034.474(14)	-0.006	1.0
6-5	2.5	7.5 - 6.5	240 051.506(26)	-0.042	1.0
6-5	2.5	6.5 - 5.5	240 066.382(6)	0.018	1.0
6-5	2.5	5.5 -4.5	240 078 266(0)	0.040	O Obcd
6-5	1.5	4.5-3.5	240 078.200(9)	0.949	0.0
6-5	2.5	3.5 - 2.5	240 090.374(47)	0.269	0.0^{b}
6-5	1.5	7.5-6.5	240 043.508(15)	-0.052	1.0
6-5	1.5	6.5 - 5.5	240 057.153(27)	0.027	1.0
6-5	1.5	5.5 - 4.5	240 069.010(22)	0.018	1.0
6-5	0.5	6.5-5.5	240 052.444(32)	0.009	1.0
6-5	0.5	5.5 - 4.5	240 064.102(21)	0.009	1.0
7-6	2.5	9.5-8.5	280 033.178(31)	0.026	1.0
7-6	2.5	8.5-7.5	280 044.814(38)	-0.038	1.0
7-6	2.5	7.5-6.5	290.055.295(10)	0.026	1.00
7-6	0.5	6.5-5.5	280 055.585(10)	0.036	1.0*
7-6	2.5	6.5 - 5.5	280 063.363(21)	-0.003	1.0
7-6	2.5	5.5 - 4.5	280 069.226(30)	0.093	0.0^{b}
7-6	2.5	4.5-3.5	280 073.679(33)	0.097	0.0^{b}
7-6	1.5	8.5-7.5	280 040.111(52)	0.029	1.0
7-6	1.5	7.5-6.5	280 049.449(26)	-0.027	1.0
7-6	1.5	6.5-5.5	280 057.917(19)	-0.024	1.0
7-6	1.5	5.5 - 4.5	280 064.560(45)	0.014	1.0
7-6	0.5	7.5-6.5	280 046.742(17)	0.025	1.0
8-7	2.5	10.5-9.5	320 022.399(18)	-0.016	1.0
8-7	2.5	9.5-8.5	320 030.916(14)	0.018	1.0
8-7	2.5	8.5-7.5	320 038.622(14)	-0.062	0.0^{b}
8-7	2.5	7.5-6.5	320 044.752(10)	-0.005	1.0
8-7	2.5	6.5-5.5	320 049.171(14)	-0.029	1.0
8-7	2.5	5.5-4.5	320 053.126(4)	-0.023	1.0
8-7	1.5	9.5-8.5	320 027.866(14)	-0.009	1.0
8-7	1.5	8.5-7.5	320 034.769(13)	0.015	1.0
8-7	1.5	7.5-6.5	320 041.079(20)	0.075	0.0^{b}
8-7	1.5	6.5-5.5	320 046.573(12)	-0.011	1.0
8-7	0.5	8.5-7.5	320 033.014(14)	0.000	1.0
8-7	0.5	7.5-6.5	320 039.803(9)	-0.004	1.0
9-8	2.5	11.5 - 10.5	360 001.929(6)	0.008	1.0
9-8	2.5	10.5-9.5	360 008.365(11)	0.026	1.0
9-8	2.5	7.5-6.5	360 022.641(16)	0.025	1.0
9-8	2.5	6.5-5.5	360 026.009(6)	-0.075	0.0^{b}
9-8	1.5	10.5-9.5	360 006.335(10)	0.006	1.0
9-8	1.5	9.5-8.5	360 011.638(5)	0.050	1.0
9-8	1.5	7.5-6.5	360 021.111(21)	-0.013	1.0
9-8	0.5	9.5-8.5	360 010.391(4)	-0.032	1.0
10-9	2.5	12.5 - 11.5	399 970.965(15)	-0.027	1.0
10-9	2.5	11.5 - 10.5	399 976.036(13)	0.023	1.0
10-9	2.5	10.5-9.5	399 980.691(32)	-0.101	0.0^{b}
10-9	2.5	9.5-8.5	399 984.621(31)	0.012	1.0
10-9	2.5	7.5-6.5	399 990.460(21)	-0.031	1.0
10–9	1.5	11.5-10.5	399 974.493(20)	-0.127	0.0^{b}
10-9	1.5	10.5-9.5	200 079 270(12)	0.007	1.00
10-9	0.5	10.5-9.5	377 710.312(13)	0.007	1.0
10-9	1.5	9.5-8.5	200 002 500(22)	0.010	1.00
10-9	0.5	9.5-8.5	399 982.500(33)	-0.012	1.0

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

^aThe numbers in parentheses represent the variances of the observed value in units of the last significant digits.

^bNot included in the fit.

^cOverlap of two NCl spectra lines.

^dNot accurately measured due to the disturbance.

$$H_{\rm hfs} = a(\rm Cl)I_{\rm Cl} \cdot L + a(\rm N)I_{\rm N} \cdot L + H_{\mathcal{Q}}(\rm Cl) + H_{\mathcal{Q}}(\rm N) + C_{\rm I}(\rm Cl)I_{\rm Cl} \cdot (J-L) + C_{\rm I}(\rm N)I_{\rm N} \cdot (J-L).$$
(3)

Here H_0 represents nuclear-quadrupole interaction. How-

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TABLE III. Matrix elements for the hyperfine Hamiltonian of the ${}^{1}\Delta$ state.^a

$$\langle I_{l}I_{2}G'J'\Lambda FM_{F}|a(1)I_{1} \cdot L|I_{l}I_{2}GJ\Lambda FM_{F}\rangle = (-1)^{J+I_{1}+I_{2}+G'+G+F+1} \begin{bmatrix} F & G' & J' \\ 1 & J & G \end{bmatrix} \begin{bmatrix} I_{1} & G' & I_{2} \\ G & I_{1} & 1 \end{bmatrix} \begin{bmatrix} I_{1}(I_{1}+1)(2I_{1}+1)(2G'+1)(2G'+1)(2J'+1)(2J'+1) \end{bmatrix}^{1/2} \\ \times (-1)^{J'-\Lambda} \begin{pmatrix} J' & 1 & J \\ -\Lambda & 0 & \Lambda \end{pmatrix} \Lambda a(1) \\ \langle I_{1}I_{2}G'J'\Lambda FM_{F}|a(2)I_{2} \cdot L|I_{1}I_{2}GJ\Lambda FM_{F}\rangle = (-1)^{J+I_{1}+I_{2}+2G'+F+1} \begin{bmatrix} F & G' & J' \\ 1 & J & G \end{bmatrix} \begin{bmatrix} I_{2} & G' & I_{1} \\ G & I_{2} & 1 \end{bmatrix} \begin{bmatrix} I_{2}(I_{2}+1)(2I_{2}+1)(2G'+1)(2G'+1)(2G'+1)(2G'+1) \\ \times (2J'+1)(2J+1) \end{bmatrix}^{1/2} (-1)^{J'-\Lambda} \begin{pmatrix} J' & 1 & J \\ -\Lambda & 0 & \Lambda \end{pmatrix} \Lambda a(2) \\ \langle I_{1}I_{2}G'J'\Lambda FM_{F}|H_{Q}(1)|I_{1}I_{2}GJ\Lambda FM_{F}\rangle = (-1)^{J+I_{1}+I_{2}+G'+G+F} \begin{bmatrix} F & G' & J' \\ 2 & J & G \end{bmatrix} \begin{bmatrix} I_{1} & G' & I_{2} \\ G & I_{1} & 2 \end{bmatrix} \begin{bmatrix} (I_{1}+1)(2I_{1}+1)(2I_{1}+3) \\ I_{1}(2I_{1}-1) \end{bmatrix}^{1/2} \\ \langle I_{1}I_{2}G'J'\Lambda FM_{F}|H_{Q}(2)|I_{1}I_{2}GJ\Lambda FM_{F}\rangle = (-1)^{J+I_{1}+I_{2}+2G'+F} \begin{bmatrix} F & G' & J' \\ 2 & J & G \end{bmatrix} \begin{bmatrix} I_{2} & G' & I_{1} \\ G & I_{2} & 2 \end{bmatrix} \begin{bmatrix} (I_{2}+1)(2I_{2}+1)(2I_{2}+3) \\ I_{2}(2I'-1) \end{bmatrix}^{1/2} \\ \langle I_{1}I_{2}G'J'\Lambda FM_{F}|H_{Q}(2)|I_{1}I_{2}GJ\Lambda FM_{F}\rangle = (-1)^{J+I_{1}+I_{2}+2G'+F} \begin{bmatrix} F & G' & J' \\ 2 & J & G \end{bmatrix} \begin{bmatrix} I_{2} & G' & I_{1} \\ G & I_{2} & 2 \end{bmatrix} \begin{bmatrix} I_{1}(I_{1}+1)(2I_{2}+1)(2I_{2}+3) \\ I_{2}(2I'-1) \end{bmatrix}^{1/2} \\ \langle I_{1}I_{2}G'J'\Lambda FM_{F}|H_{us}(1)|I_{1}I_{2}GJ\Lambda FM_{F}\rangle = (-1)^{J+I_{1}+I_{2}+2G'+F} \begin{bmatrix} F & G' & J' \\ 1 & J & G \end{bmatrix} \begin{bmatrix} I_{2} & G' & I_{1} \\ G & I_{1} & 1 \end{bmatrix} \begin{bmatrix} I_{1}(I_{1}+1)(2I_{1}+1)(2G'+1)(2G+1) \end{bmatrix}^{1/2} \\ \langle I_{1}I_{2}G'J'\Lambda FM_{F}|H_{us}(2)|I_{1}I_{2}GJ\Lambda FM_{F}\rangle = (-1)^{J+I_{1}+I_{2}+2G'+F+1} \begin{bmatrix} F & G' & J' \\ 1 & J & G \end{bmatrix} \begin{bmatrix} I_{2} & G' & I_{1} \\ G & I_{2} & 1 \end{bmatrix} \begin{bmatrix} I_{2}(I_{2}+1)(2I_{2}+1)(2G+1) \end{bmatrix}^{1/2} \\ \times \begin{bmatrix} \delta_{J'}I_{J}(J(J+1)(2J+1)]^{1/2} - [(2J'+1)(2J+1)]^{1/2} (-1)^{J'-\Lambda} \begin{pmatrix} J' & 1 & J \\ -\Lambda & 0 & \Lambda \end{pmatrix} \Lambda \end{bmatrix} C_{I}(1) \\ \langle I_{1}I_{2}G'J'\Lambda FM_{F}|H_{us}(2)|I_{1}I_{2}GJ\Lambda FM_{F}\rangle = (-1)^{J+I_{1}+I_{2}+2G'+F+1} \begin{bmatrix} F & G' & J' \\ 1 & J & G \end{bmatrix} \begin{bmatrix} I_{2} & G' & I_{1} \\ G & I_{2} & 1 \end{bmatrix} \begin{bmatrix} I_{2}(I_{2}+1)(2I_{2}+1)(2G+1) \end{bmatrix}^{1/2} \\ \times \begin{bmatrix} \delta_{J'}I_{J}(J(J+1)(2J+1)]^{1/2} - [(2J'+1)(2J+1)]^{1/2} (-1)^{J'-\Lambda} \begin{pmatrix} J' & 1 & J \\ -\Lambda & 0 & \Lambda \end{pmatrix} \Lambda \end{bmatrix} C_{I}(2) \\ \times \begin{bmatrix} \delta_{J'}I_{$$

^aCoupling scheme of the angular momenta is as follows: $G = I_1 + I_2$, F = J + G. For NCl $(a^{-1}\Delta)$, I_1 and I_2 corresponds to I_{Cl} and I_N , respectively.

ever, we found that the above coupling scheme does not hold well for the $a {}^{1}\Delta$ state of NCl, and F_{1} is not a good quantum number. In fact, we had difficulty in assigning several weak components of the hyperfine structure. This is because hyperfine interactions due to the nitrogen and chlorine nuclei have nearly the same orders of magnitude, as suggested by the hyperfine spectral pattern shown in Fig. 1. Therefore, we adopted the following coupling scheme of the angular momenta:

$$G = I_{\rm Cl} + I_{\rm N} \tag{4}$$

and

$$F = J + G. \tag{5}$$

The matrix elements of the Hamiltonian given above were derived by the standard spherical-tensor formalism.²⁴ The derived elements were summarized in Table III. In this coupling scheme, $\Delta G = 0$ and $\Delta F = \pm 1,0$ transitions are allowed. A least-squares fit program was written for the ¹ Δ state having two nuclei with different spins.

An initial guess of hyperfine coupling constants and nuclear electric quadrupole coupling constants was made from a comparison of the corresponding constants for NCl($X^{3}\Sigma^{-}$)⁹ and NF($a^{1}\Delta$).⁵ Then, definite assignments for hyperfine components were made on the basis of the predicted

spectral patterns. Finally, the 70 observed spectral lines for v=0 and 49 lines for v=1 were analyzed to determine molecular constants by the least-squares method. The nuclear spin-rotation constant of the nitrogen nucleus was found to be smaller than that of the chlorine nucleus by one order of magnitude so that it was fixed to be zero in the final analysis. The standard deviations of the final fit for the v=0 and the v=1 transitions were 21 and 24 kHz, respectively, which could be compared with frequency measurement errors, as shown in Table I and Table II. The molecular constants for the ground vibrational state and the first excited state are listed in Table IV.

DISCUSSION

In the previous studies it was reported that the reaction of the chlorine atom with the molecular azide was essential to produce the NCl radical in the $a^{-1}\Delta$ state. However, we found that a simple dc-glow discharge of a mixture of Cl₂ and N₂ gives a reasonable amount of the radical in the $a^{-1}\Delta$ state in the plasma. The NCl($a^{-1}\Delta$) radical is generated from N(²D) and Cl(²P) when produced by three-body reaction of atoms, while NCl($X^{-3}\Sigma^{-1}$), from N(⁴S) and Cl(²P).¹⁹ Larger currentand higher pressure may be linked with the sufficient production of N(²D) other than the production by a simple

TABLE IV. Molecular constants of NCl $(a \ ^1\Delta)$ (MHz).^a

υ	0	1
В	20 196.298 60(160)	20 007.6252(24)
D	0.045 238 1(112)	0.0450 240(166)
a(Cl)	102.515(152)	101.48(36)
a(N)	91.43(21)	91.53(38)
eQq(Cl)	-52.54(68)	-54.07(144)
eQq(N)	1.72(46)	2.07(84)
$C_I(Cl)$	0.0196(99)	0.0159(165)

^aThe numbers in parentheses represent three standard deviations in units of the last significant digits.

excitation of NCl($X^{3}\Sigma^{-}$) to NCl($a^{1}\Delta$) by discharge. Better production with a shorter cathode length indicates that an even smaller area of the metal electrode may somewhat disturb the recombination of the nitrogen and chlorine atoms or the quenching of NCl($a^{1}\Delta$) to the ground electronic state.

Using the following relation²³ by assuming Morse function as an internuclear potential:

$$\alpha_e = 6 \sqrt{\frac{\chi_e B_e^3}{\omega_e} - \frac{6B_e^2}{\omega_e}}, \tag{6}$$

we estimated the rotation-vibration coupling constant α_e to search for lines in the v=1 state with $\omega_e \chi_e$ obtained from infrared emission spectroscopy.¹⁵ However α_e was found to be underestimated. On the other hand, since B_e^2/ω_e^2 is small enough, Dunham expansion²⁵ is applicable. By assuming Y_{11} and Y_{20} to be $-\alpha_e$ and $-\omega_e \chi_e$, cubic and quartic internuclear potential constants, a_1 and a_2 were determined to be -3.1 and 7.2 for NCl($a^{-1}\Delta$). By these constants, β_{e} was calculated to be -0.000 44 MHz. The experimental value of our study was $-0.000\ 214(20)$ MHz which is the same order of magnitude and thought to be reasonable. This is caused by relatively large value of a_2 to a_1 . The small difference between a_1 and a_2 decides the sign of β_e . If Morse potential was assumed, β_e should be a positive value. Both results, the underestimation of α_e and the negative value of β_e , indicate that the Morse potential is not a good approximation in this case.

Since molecular constants of NCl($a^{1}\Delta$) in the v=0 and v=1 levels were determined in the present study, equilibrium parameters are derived as shown in Table V where vibrational parameters by infrared emission spectroscopy¹⁵ are also given. The equilibrium bond length, r_e , is determined to be 1.578 272 6(20) Å. The three standard errors in Planck's constant and the atomic mass unit²⁶ are included in error estimation. The bond length from an *ab initio* MO calculation¹⁷ at the estimated full configuration interaction level, is 1.598 Å, which is slightly larger than our result. The vibrational frequency given by infrared emission spectroscopy¹⁵ also agrees well with our more accurate value of 905.498(187) cm⁻¹ derived by a well-known relation, $D_e = 4B_e^{3}/\omega_e^2$.

The spin density and hyperfine constants of each nucleus are summarized in Table VI together with those of NCl($X^{3}\Sigma^{-}$).⁹ The spin density of each nucleus was evaluated from the ratio of hyperfine constants, *a* to the atomic

TABLE V. Equilibrium structural parameters of NCl ($a^{-1}\Delta$).^a

	This study	Infrared emission ^b
B_e (MHz)	20 290.6353(27)	
D_e (MHz)	0.045 345 2(187)	
$\alpha_e(\text{MHz})$	188.6734(29)	
β_e (MHz)	$-0.000\ 214(20)$	
$\omega_e (\mathrm{cm}^{-1})^{\mathrm{c}}$	905.498(187)	904(18)
$\omega_e \chi_e \ (\mathrm{cm}^{-1})^{\mathrm{d}}$	6.392 99(178)	4.7(36)
r_e (Å)	1.578 272 6(20)	

^aThe numbers in parentheses represent three standard deviations in units of the last significant digits.

^bReference 15. ^cDerived by the following relation, $D_e = 4B_e^3/\omega_e^2$.

^dDerived by the following relation, $\alpha_e = (6B_e^2/\omega_e)[(\omega_e\chi_e/B_e)^{1/2} - 1]$ by assuming Morse potential.

value.²⁷ It is to be noted that the total spin density of NCl($a^{1}\Delta$) is less than 90%. The spin densities of the $a^{1}\Delta$ state and the $X^{3}\Sigma^{-}$ state are quite similar, though these evaluations by the orbital average and the spin average include at least 15% difference.²⁸ This hampers a detailed discussion on the spin density change in NCl by electronic excitation. We can only say that the spin density of NCl($a^{1}\Delta$) is nearly the same as that of NCl in the ground electronic state.

The ionic character of Cl was estimated from the quadrupole coupling constant of the Cl nucleus. The increase in the ionic character from NCl($X^{3}\Sigma^{-}$) to NCl($a^{1}\Delta$) is consistent with the decrease in the bond length: $r_{e}=1.610705(19)$ Å for $X^{3}\Sigma^{-}$ (Ref. 11) to $r_{e}=1.5782726(20)$ Å for $a^{1}\Delta$. The quadrupole coupling constant of the N nucleus is equal to that of the ground state within experimental uncertainties. This is because the change in the small absolute value is difficult to distinguish. The differences in the hyperfine parameters between v=0 and v=1 were small and marginal.

While the nuclear spin rotation coupling constant of the Cl nucleus, $C_I(Cl)$, was determined, that of the N nucleus, $C_I(N)$, could not be determined in the present study. The nuclear spin rotation coupling constant are estimated by the second-order perturbation in the same manner as NF($a^{-1}\Delta$).⁵

$$C_I = \frac{4Ba}{\Delta E}.$$
(7)

 ΔE represents an energy difference between the $a^{-1}\Delta$ state and the nearest perturbing state. From $C_I(Cl)$, this energy difference is calculated to be ca. 1.8 eV. To the best of our

TABLE VI. Hyperfine constants of each nucleus and derived parameters.

	$NCl(a^{-1}\Delta)v=0$	NCl($X^{3}\Sigma^{-}$)	
Spin density on the N atom	0.659	0.758 ^a	
Spin density on the Cl atom	0.234	0.219 ^a	
Electron transfer Δ_p	0.47	0.44	
eQq(N) (MHz)	1.72	1.842	
eQq(Cl) (MHz)	-52.54	-63.13	
Ionic character i_c	0.29	0.21	
$C_I(\text{Cl})$ (MHz)	0.0196	0.0152	
	This study	Ref. 9	

^aCalculated from -(5/3)c.

knowledge, no corresponding electronic state is reported even in the references on quantum chemical calculations. By using this value, $C_I(N)$ is calculated to be 0.017 MHz. As our fitting results suggested that $C_I(N)$ is smaller than $C_I(Cl)$ by one order of magnitude, estimated $C_I(N)$ is too large compared to our result. This discrepancy may be due to a cancellation by the second term of nuclear-spin rotation interaction which is a term of charge distribution about the nucleus concerned.²⁵

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