Microwave Spectrum of NCl in the Second Electronically Excited State (b $^1\Sigma^+$)

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The pure rotational transitions of $N^{35}Cl$ in the second electronically excited state, b $^1\Sigma^+$, were detected together with those of the isotopic species $N^{37}Cl$ by microwave spectroscopy. The NCl radical in the b $^1\Sigma^+$ state was generated by dc-glow discharge of a N_2/Cl_2 mixture. The rotational constant, centrifugal distortion constant, and quadrupole coupling constants of the Cl nucleus were determined. The observation of rotational transitions in the vibrationally excited $v = 1$ state made it possible to derive equilibrium structural parameters. A discussion on the internuclear potential of the three low-lying electronic states of NCl is given.

Introduction

The difficulty in producing molecules in metastable electronic states has prevented the observation of pure rotational spectra of such species. This is especially true for molecules in the second electronically excited state since microwave spectra have only been observed for CO(b $^3\Sigma^+$)[1] and SO(b $^1\Sigma^+$)[2]. Other than these examples, some reports on molecules in the first electronically excited state, that is, SO(a $^1\Delta$)[3−5], O_2(a $^1\Delta_g$)[6], CO(a $^3\Pi$)[7], NF(a $^1\Delta$)[8], and NCl(a $^1\Delta$)[9], are known. In these electronic systems, i.e. $X^3\Sigma^-$, a $^1\Delta$, and b $^1\Sigma^+$, these results clearly reflect that b $^1\Sigma^+-X^3\Sigma^-$ transition is weakly allowed via the magnetic dipole selection rule whereas the a $^1\Delta-X^3\Sigma^-$ transition is spin and orbital forbidden.

The b $^1\Sigma^+$ state of NCl was first identified in the b $^1\Sigma^+-X^3\Sigma^-$ electronic spectrum.[10] From the b−X electronic emission spectrum, vibrational and rotational constants of both states were determined and the low-lying electronic state, b $^1\Sigma^+$ was shown to be 15 038.94 cm^{-1} above the $X^3\Sigma^-$ ground state. Yamada and his collaborators[11−13] studied the microwave spectrum of NCl($X^3\Sigma^-$) by using dc-glow discharge of a nitrogen and chlorine gaseous mixture. They determined its detailed molecular constants and derived the spin densities of the unpaired electrons for the nitrogen and chlorine atoms. The data of the b−*X* electronic transition obtained by Colin and Jones[10] were reanalyzed with the precise molecular constants of NCl($X^3\Sigma^-$). The radiative life time of NCl(b $^1\Sigma^+$) was reported to be 0.25 ms when generated by mild microwave discharge,[14] which was shorter than that (2 ms) of NCl(a $^1\Delta$). These lifetimes are consistent with the nature of the electronic transitions, as described above.

The azide radical reaction

$$N_3 + Cl \rightarrow NCl(a\ ^1\Delta,\ b\ ^1\Sigma^+) + N_2$$

is an efficient method of generating metastable NCl radical,[15,16] which was thought to be an important point. The a−X emission spectra were measured in the near infrared region using this reaction[17] and many studies on the kinetics of NCl were carried out. Our recent microwave study of NCl(a $^1\Delta$)[9], however, showed that dc-glow discharge of an N_2 and Cl_2 mixture is also an effective production method. Recent development of chemical laser systems utilizing transient species like NCl(a $^1\Delta$) forwarded research on the quenching constants. Ray and Coombe[18] studied collisional quenching rates of NCl(a $^1\Delta$) with several molecules. NCl(b $^1\Sigma^+$) quenching rate constants were determined by several groups.[19,20] The molecular properties of NCl concerning its geometrical structure,[21] electronic structure,[22,23] and radiative lifetime[24,25] were studied by several *ab initio* MO calculations.

In the present study we have detected the pure rotational spectra of NCl(b $^1\Sigma^+$) in the $v = 0$ and $v = 1$ states and determined molecular constants and a precise equilibrium structure. This report completes microwave spectra of the NCl radical in the three low-lying states. The result is a good example of how the molecular structure and potential energy surface change between electronic states.

Experimental Section

The source-modulated microwave spectrometer attached to a 2 m free-space cell at the Institute for Molecular Science was used for the experiment. The experimental setup has been described in a previous report.[26] The experimental conditions were similar to those used for observing the microwave spectrum of NCl(a $^1\Delta$). NCl(b $^1\Sigma^+$) was produced by a dc-glow discharge of nitrogen gas (7 m Torr) and chlorine gas (9.98% diluted in helium gas, 20 mTorr). The discharge current was 200 mA. The background pressure was 3 mTorr, and the 2 m free-space cell was maintained between 180 and 200 K by circulating liquid nitrogen in the cooling jacket during the measurements.

First we searched for the $N = 9-8$ diamagnetic transition line in 368 GHz region predicted from the rotational constant and the centrifugal distortion constant obtained from the reanalysis[11] of the b−X electronic transition. A diamagnetic line was detected near predicted frequency. Since NCl in the b $^1\Sigma^+$ state is diamagnetic, the Zeeman effect can not be applicable to the discrimination of lines due to various diamagnetic reaction intermediates and products. The line immediately disappeared when discharge was turned off or nitrogen gas or chlorine gas flow was cut off. Eight series lines were found in the 164−450 GHz region in total. The lowest two rotational lines with $N = 4-3$ and $N = 5-4$ show hyperfine structure due to the chlorine nucleus, as shown in Figure 1. The observation of the $N = 9-8$ transition of the isotopic species, $N^{37}Cl$(b $^1\Sigma^+$), in the 363 GHz region in natural abundance confirmed that these series lines are due to $N^{35}Cl$(b $^1\Sigma^+$). Four rotational lines of $N^{37}Cl$(b $^1\Sigma^+$) were also measured. For a further confirmation of the spectral lines in the b $^1\Sigma^+$ state, spectral lines of $N^{35}Cl$(b $^1\Sigma^+$) in the $v = 1$ vibrationally excited state were searched for. A somewhat weaker dia-

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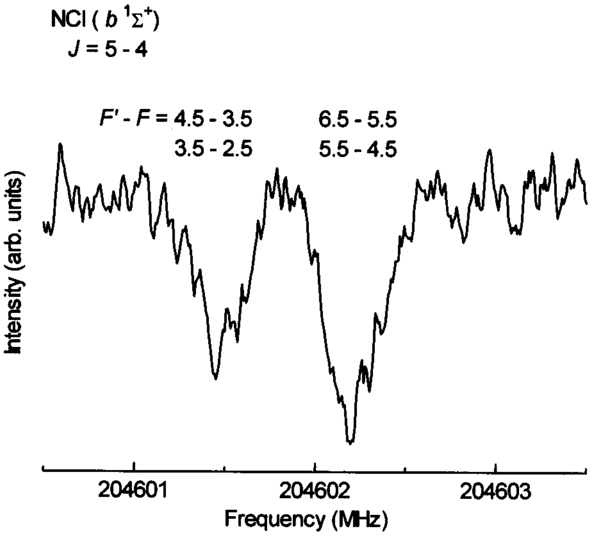

Figure 1. The $J = 5-4$ transition line in the $v = 0$ state of NCl(b $^1\Sigma^+$). The splitting due to the quadrupole interaction of the chlorine nucleus was observed. The NCl radical was generated by a dc-glow discharge in a gaseous mixture of N_2 and Cl_2 (9.98% dispersed in helium gas) at a total pressure of 30 mTorr. The integration time was 80 s.

magnetic line compared with that of the ground vibrational state was observed. By the difference of these two lines, α_e was estimated and five additional $v = 1$ lines were observed on the basis of the calculated frequencies. The estimated vibrational temperature was 1800 K under the experimental conditions.

Results and Discussion

The observed lines were analyzed by using a conventional Hamiltonian for a diatomic molecule in the $^1\Sigma^+$ state with electronic quadrupole coupling interaction of the chlorine nucleus. The observed lines of both isotopic species are listed in Table 1. The molecular constants of $N^{35}Cl$ and $N^{37}Cl$ obtained from the least-squares fit are summarized in Table 2 with the data of $N^{35}Cl$ obtained from the study on electronic emission spectroscopy. The molecular constants obtained in the present study agree well with the constants obtained from the electronic spectroscopy. However, our results provide improved accuracy. The standard deviations of the final fit of $N^{35}Cl$ in the $v = 0$ and $v = 1$ states and $N^{37}Cl$ in the $v = 0$ state were 30, 43, and 36 kHz, respectively, which fall within the experimental errors, as shown in Table 2.

The equilibrium parameters of $N^{35}Cl$(b $^1\Sigma^+$) derived from the molecular constants of the $v = 0$ and $v = 1$ states are shown in Table 3. For comparison equilibrium parameters of the other two low-lying electronic states are also shown in Table 3. The equilibrium bond length, r_e, is determined to be 1.568 006 9(20) Å, where the precision of the calculated bond length is limited by the experimental accuracy of Planck's constant and the atomic mass unit.[27] On the other hand, the bond length obtained from *ab initio* MO calculation[23] by the full configuration interaction (F-CI) method is 1.598 Å, which is slightly larger than our value. The bond length of the b $^1\Sigma^+$ state obtained by the F-CI method has the same value as that of the a $^1\Delta$ state. However, the results of other calculation methods showed that the bond length of the b $^1\Sigma^+$ state is always smaller than that of the a $^1\Delta$ state. The decrease in bond length from the $X^3\Sigma^-$ state to the b $^1\Sigma^+$ state is the same as the result of previous *ab initio* MO calculations and well corresponds to the increasing tendency of vibrational frequency. These tendencies suggest that the NCl bond acquires more double-bond character in the a and b electronic states. This picture is also consistent with the decrease in the quadrupole coupling constant of the C1 nucleus if the amount of π electron back-donation increases from the $X^3\Sigma^-$ state to the b $^1\Sigma^+$ state. This back-donation is supported by the net Mulliken charge of the nitrogen nucleus obtained by Papakondylis and his co-workers in their *ab initio* MO study.[23] They showed the decrease in the charge of the N nucleus from $-0.08(\chi^3\Sigma^-)$ to -0.20(b $^1\Sigma^+$) at the CISD level of theory. The change in the bond length and vibrational frequency in the single bond of NCl from the $^3\Sigma^-$ state to the $^1\Sigma^+$ state makes a distinct contrast with the one in the double-bonded radicals such as SO, which has an isoelectronic system.[2] The vibrational frequency given by electronic spectra also agrees well with our more accurate value of 936.75(99) cm^{-1}.

TABLE 1: Observed Rotational Transitions of NCl(b $^1\Sigma^+$)[a]

$N'-N$	$F'-F$	ν_{obs} (MHz)	$\Delta\nu$(obs − calc) (MHz)	weight
		$N^{35}Cl$ $v = 0$		
4−3	5.5−4.5 4.5−3.5	163 688.416(29)	−0.004	1.0
	3.5−2.5 2.5−1.5	163 686.946(50)	0.025	1.0
5−4	6.5−5.5 5.5−4.5	204 602.392(14)	0.010	1.0
	4.5−3.5 3.5−2.5	204 601.452(44)	−0.044	1.0
6−5		245 510.950(20)	0.083	0.0[d]
7−6		286 413.376(31)	0.034	1.0
8−7		327 308.398(15)	−0.016	1.0[b]
9−8		368 195.041(19)	0.011	1.0
10−9		409 072.104(9)	−0.030	1.0
11−10		449 938.688(9)	0.017	1.0
		$v = 1$		
6−5		243 236.282(25)	0.033	1.0
7−6		283 759.465(48)	−0.182	0.0[b,d]
8−7		324 275.668(25)	0.014	1.0
9−8		364 783.162(24)	−0.056	1.0
10−9		405 281.272(42)	−0.014	1.0
11−10		445 768.833(11)	0.030	1.0
		$N^{37}Cl$ $v = 0$		
7−6		282 000.635(48)	0.029	1.0
8−7		*c*		0.0[d]
9−8		362 522.988(20)	−0.027	1.0
10−9		402 770.875(18)	−0.022	1.0
11−10		443 008.553(22)	0.024	1.0

[a] The numbers in parentheses represent the variances of the observed value in units of the last significant digits. [b] Not accurately measured due to the interfering line. [c] Not observed due to the interfering line. [d] Not included in the fit.

In the Dunham expansion, the internuclear potential is assumed to be of the form

$$U = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + ...) \tag{3}$$

where

$$\xi = \frac{r - r_e}{r_e} \tag{4}$$

From the observed equilibrium constants, Dunham expansion coefficients are evaluated. These parameters are tabulated in Table 4 with the data of the SO radical.[2,5,28,29] The shape of potential is governed by a_1 and a_2. Near the equilibrium geometry, we can see that the shapes of potential resemble each other which suggests that the change of spin states does not affect the shape of each potential. The strength of the bond is indicated by a_0. It is interesting to notice that the change of spin orientation decreases the total energy of the NCl and SO

TABLE 2: Molecular Constants of NCl(b $^1\Sigma^+$) (MHz)[a]

	present study			electronic transition[b]
	$N^{35}Cl$		$N^{37}Cl$	$N^{35}Cl$
v	0	1	0	0
B_v	20 462.412 4(53)	20 272.855 8(115)	20 147.0853(119)	20 462.84(153)
D_v	0.044 026(30)	0.043 955(61)	0.042 702(60)	0.044 25(144)
eQq(Cl)	−51.7(36)	−51.7[c]	0[c]	*d*
rms	0.030	0.043	0.036	

[a] The numbers in parentheses represent 3 standard deviations in units of the last significant digits. [b] Reference 11. Converted from cm^{-1} units to MHz units. [c] Fixed value. [d] Not determined.

TABLE 3: Equilibrium Molecular Constants of $N^{35}Cl$[a]

	NCl($X^3\Sigma^-$)[b]	NCl(a $^1\Delta$)[c]	NCl(b $^1\Sigma^+$)[d]	NCl(b $^1\Sigma^+$)[e]
B_e (MHz)	19 481.734(144)	20 290.635 3(27)	20 557.190 7(98)	
α_e (MHz)	192.297(21)	188.673 4(29)	189.556 6(127)	
D_e (MHz)	0.047 912(64)	0.045 345 2(187)	0.044 062(93)	
β_e (MHz)	−0.000 050(32)	−0.000 214(20)	−0.000 071(68)	
ω_e (cm^{-1})	827.957 8(26)[f]	905.498(187)[f]	936.75(99)[f]	935.6
$\omega_e\chi_e$ (cm^{-1})	5.300 2(21)[g]	5.274(50)[g]	5.777(181)[g]	5.4
r_e (Å)	1.610 705(19)	1.578 272 6(20)	1.568 006 9(20)	
eQq(N) (MHz)[h]	1.842(96)	1.72(46)	*i*	
eQq(Cl) (MHz)[h]	−63.13(18)	−52.54(68)	−51.7(36)	

[a] The numbers in parentheses represent 3 standard deviations in units of the last significant digits. [b] References 11 and 13. B_e, α_e, D_e, β_e, ω_e, and $\omega_e\chi_e$ were assumed to be Y_{01}, $-Y_{11}$, Y_{02}, Y_{12}, Y_{10}, and $-Y_{20}$ respectively. Some constants were converted from cm^{-1} units to MHz units. [c] Reference 9. [d] Present study. [e] Reference 10. Electronic transition. [f] Derived by the following relation, $D_e = 4B_e^3/\omega_e^2$. [g] Derived by Dunham expansion coefficients shown in Table 4. [h] These values are those of the ground vibrational state. [i] Not determined.

TABLE 4: Potential Parameters of $N^{35}Cl$ and SO[a]

	NCl($X^3\Sigma^-$)[b,c]	NCl(a $^1\Delta$)[b,d]	NCl(b $^1\Sigma^+$)[e]
a_0 (cm^{-1})	263 723.88(162)	302 859(125)	319 922(676)
a_1	−3.096 02(23)	−3.073 37(43)	−3.099 5(22)
a_2	6.544 2(27)	6.612(49)	6.392(176)
	SO($X^3\Sigma^-$)[f]	SO(a $^1\Delta$)[b,g]	SO(b $^1\Sigma^+$)[b,h]
a_0 (cm^{-1})	459 187(26)	435 965(190)	406 385(257)
a_1	−3.122 22(15)	−3.209 91(52)	−3.299 13(73)
a_2	6.312 7(141)	6.945(188)	6.733(69)

[a] The numbers in parentheses represent three standard deviations in units of the last significant digits. [b] These parameters are derived from the experimental values taken from the references by using the Dunham expansion. [c] Reference 11. [d] Reference 9. [e] Present study. [f] Reference 28. [g] References 5 and 29. [h] Reference 2.

radicals from the b $^1\Sigma^+$ state to the $X^3\Sigma^-$ state, while it decreases the bond strength of NCl and increases that of SO. This may be concerned with the picture that unpaired electrons mainly occupy $2p_x$ and $2p_y$ orbitals of the N atom in NCl while they mainly occupy hybrid orbitals between S and O in SO. For further understanding of bond nature and quadruple coupling constants, more accurate quantum chemical calculation are required.

Although the radiative lifetime of the b $^1\Sigma^+$ state (0.25 ms) is about one-eighth of that of the a $^1\Delta$ state, the intensity ratio of NCl(b $^1\Sigma^+$) for $N = 9-8$ to NCl(a $^1\Delta$) for $J = 9-8$ was 0.05−0.1 depending on its production condition. This result suggests that the microwave line intensity does not depend only on the radiative lifetime as Yamamoto pointed out in the report on SO(b $^1\Sigma^+$)[2] but also on the collisional decay process. The decay kinetics of NCl(a $^1\Delta$, b $^1\Sigma^+$) with several gases was thoroughly studied[18−20] showing large dependency on the quenching gas. Comparing the quenching rates of NCl(a $^1\Delta$) and NCl(b $^1\Sigma^+$) with several molecules which are thought to have been present in the discharge cell, NCl(a $^1\Delta$) has a higher quenching rate than NCl(b $^1\Sigma^+$) in most cases. The NF(b $^1\Sigma^+$) radical was searched for on the basis of the production conditions used in the study of its electronic emission spectroscopy.[30] However, no signal was observed by dc-glow discharge of NF_3 and H_2 or Ar. In case of NF, NF(b $^1\Sigma^+$)[31] has higher quenching rate than NF(a $^1\Delta$).[32] Especially the quenching rate of NF(b $^1\Sigma^+$) with F_2 is larger than that of NCl(b $^1\Sigma^+$) with Cl_2 by 2 orders of magnitude. This fact might explain our successful detection of NCl(b $^1\Sigma^+$) and failure to detect NF(b $^1\Sigma^+$) even though a strong signal was observed for NF(a $^1\Delta$).

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