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The microwave spectrum of the N ^{35}Cl radical in the $X\,^3\Sigma^-$ state

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The microwave spectrum of the N ^{35}Cl radical in the ground vibronic state has been observed by using a source frequency modulation spectrometer with a 3.5 m long free space absorption cell. The NCl radical was generated directly in the cell by a dc discharge in a mixture of N_2 and Cl_2 flowing through the cell. The electric-dipole allowed rotational transitions of N up to $4 \leftarrow 3$, each being resolved into a few spin components, were observed in the frequency region 41.5–155 GHz. Each transition was found to consist of many hyperfine components. To analyze the observed spectrum, the matrix elements of magnetic hyperfine and electric quadrupole hyperfine Hamiltonians were derived for a diatomic molecule in the triplet state of which both nuclei have nonzero spins. The rotational, spin–spin interaction, and spin-rotation interaction constants were determined to be $B = 19\,383.4655(42)$ MHz, $\lambda = 56\,390.850(16)$ MHz, and $\gamma = -208.6306(96)$ MHz, with three standard errors in parentheses. The hyperfine parameters b, c, and eQq for both the nitrogen and chlorine atoms were precisely determined together with the nuclear-spin rotation interaction constant for the chlorine atom. The spin density of the unpaired electrons was estimated to be 76% and 22%, respectively, on the nitrogen and chlorine atoms from the observed hyperfine coupling constants.

INTRODUCTION

Only a few diatomic molecules in the triplet electronic states have been investigated by microwave spectroscopy; besides a classical example of the oxygen molecule[1] three molecules have been studied: SO,[2] S_2,[3] and SeO,[4] all in the $X\,^3\Sigma^-$ state. In addition, the NH radical again in $X\,^3\Sigma^-$ has recently been investigated by far-infrared laser sideband spectroscopy.[5] The present paper reports the microwave spectrum of another triplet molecule NCl.

The first spectroscopic detection of the NCl radical was made by Milligan,[6] who photolyzed chlorine azide trapped in an argon matrix at 4.2 K and observed two infrared bands at 824 and 818 cm^{-1} with the intensity ratio of 2.5 to 2.7, which were assigned to N^{35}Cl and N^{37}Cl. Later Milligan and Jacox[7] extended the measurement and observed two more bands at 816.5 and 810 cm^{-1} which were also ascribed to the two isotopic species, but trapped in a different site of the matrix.

Briggs and Norrish[8] have reported transient absorption spectra at 2400 Å by flash photolyzing gaseous mixtures of NCl_3, Cl_2, and N_2, and have ascribed them to the NCl $^3\Pi - X\,^3\Sigma^-$ transition on a basis of photochemical arguments. By assigning the 2400 Å spectra to the (0, 0) band and the nearby continuous spectra to the (2, 0), (1, 0), and (0, 1) transitions, they estimated the vibrational frequencies of the lower and the upper states to be 870 and 550 cm^{-1}, respectively.

Colin and Jones[9] have photographed an orange afterglow downstream from a microwave discharge in a mixture of N_2 and Cl_2. The spectrum consists of double headed bands, with the strongest one at 6684.6 Å. The rotational analysis of the strongest band assigned to the 0–0 band showed that the observed spectra were due to the $b\,^1\Sigma^+ - X\,^3\Sigma^-$ transition of the NCl radical. They have obtained the vibrational and rotational constants of the upper and lower states. The lower-state $\Delta G''(1/2)$ value they determined (816.8 cm^{-1}) is in good agreement with the results of Milligan[6] and Milligan and Jacox,[7] but not with that of Ref. 8.

Yamada and Hirota[10] have recently observed a few paramagnetic absorption lines in a glow discharge in a mixture of N_2 and Cl_2 near 820 cm^{-1} using an infrared diode laser spectrometer, which they suspected to be due to NCl. This result has prompted us to detect the microwave spectrum. Since both the N and Cl atoms have the nonzero nuclear spins [$I(\mathrm{N}) = 1$ and $I(\mathrm{Cl}) = 1.5$], they may cause additional complications in the microwave spectra with triplet fine structures, but such complications, once analyzed, will provide detailed information on the unpaired-electron distributions in the molecule.

EXPERIMENTAL

The microwave spectrometer used in the present study was essentially the same as that described previously[11]; source frequency modulation with $2f$ phase sensitive detection was employed. The absorption cell was made of a Pyrex glass tube 3.5 m in length and 15 cm in diameter, and was continuously pumped by a mechanical booster pump (67 l/s) followed by a liquid nitrogen trap and a rotary pump.

The NCl radical was generated in the cell by a dc glow discharge in a 1 : 1 mixture of N_2 and Cl_2 with a total pressure of 15 to 20 mTorr. The signal-to-noise (S/N) ratio was found to be insensitive to the discharge current provided that it fell in the range of 30 to 50 mA.

At an early stage an absorption cell of 1 m length was employed, because it was expected to make the pumping speed higher. However, the S/N ratio obtained with this cell was about half of that with the 3.5 m cell. The S/N ratio for the longer cell was further increased by a factor of 3 by replacing a small (3 cm i.d.) pumping port by a large one (7.5 cm i.d.). Cooling of the cell to about

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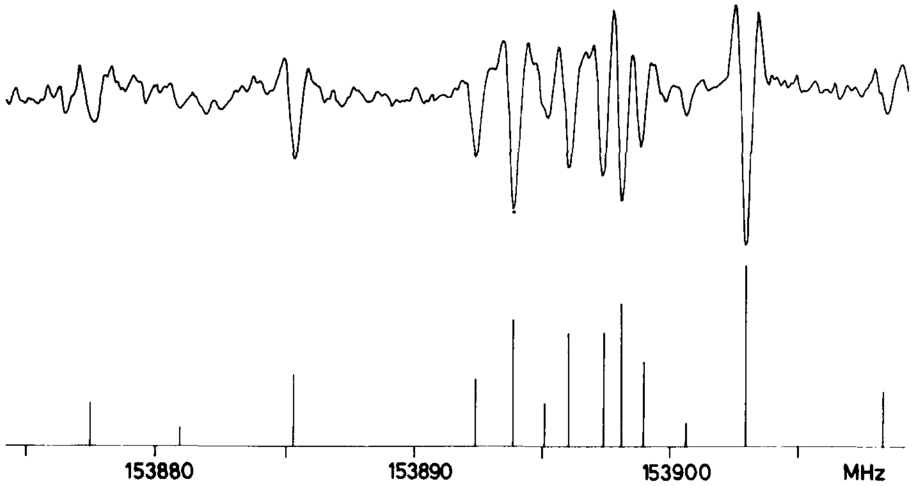

FIG. 1. The $N=4 \leftarrow 3$, $J=3 \leftarrow 2$ (F_3) transitions of NCl. The spectrum was synthesized from a few consecutive scans, each covering a region of about 10 MHz.

−100 °C was also effective in increasing the intensities of the spectral lines, especially for low-N transitions with small line strengths.

We first searched for the $N=4 \leftarrow 3$ transitions which were expected to appear around 155 GHz when Colin and Jones' constants were used. Soon after we started searching we observed three groups of lines, which almost disappeared when a magnetic field of a few tens of Gauss was applied. They were centered approximately at 155 350, 155 055, and 153 895 MHz, and were assigned to the F_1, F_2, and F_3 spin components of the $N=4 \leftarrow 3$ transition. These frequencies differed from the predicted ones by 50 to 390 MHz. The absorption lines were so strong that they were easily seen on a CRO scope. Figure 1 shows the $N=4 \leftarrow 3$, $J=3 \leftarrow 2$ (the F_3 component) transitions, synthesized from a few consecutive scans, each being about 10 MHz wide. We then proceeded to search for the $N=3 \leftarrow 2$ transitions and found again three groups of paramagnetic lines in the 116 GHz region. By using the $N=4 \leftarrow 3$ and $N=3 \leftarrow 2$ transition frequencies thus determined, the rotational and the spin–spin interaction constants were refined and were employed to predict the frequencies of the $N=2 \leftarrow 1$ and $N=1 \leftarrow 0$ transitions, which were then observed. In this way we have observed 11 electric-dipole allowed rotation/fine structure transitions, as schematically shown in Fig. 2. Each transition is further split into many hyperfine components. About 130 lines were thus measured; six independent measurements were carried out for each line with three standard deviation of 29.9 kHz.

THEORY

The Hamiltonian used in the present analysis consists of four parts:

$$\mathbf{H} = \mathbf{H}_{\mathrm{rot}} + \mathbf{H}_{\mathrm{ss}} + \mathbf{H}_{\mathrm{sr}} + \mathbf{H}_{\mathrm{hfs}}\,, \qquad (1)$$

i.e., the rotational, spin–spin interaction, spin-rotation interaction, and hyperfine interaction Hamiltonians. The following coupling scheme, Hund's case (b_β), was used for the angular momenta involved in the Hamiltonian:

$$\mathbf{J} = \mathbf{N} + \mathbf{S},\ \mathbf{F}_1 = \mathbf{J} + \mathbf{I}(\mathrm{Cl})$$

and (2)

$$\mathbf{F} = \mathbf{F}_1 + \mathbf{I}(\mathrm{N})\,,$$

where the notations are of usual meaning, except $\mathbf{F}_1$ which denotes an "intermediate" angular momentum defined by the second equation.

The matrix elements of the first three Hamiltonians in $\mathbf{H}$, $\mathbf{H}_1 = \mathbf{H}_{\mathrm{rot}} + \mathbf{H}_{\mathrm{ss}} + \mathbf{H}_{\mathrm{sr}}$, are given explicitly as follows:

$$\langle N, S, J | H_1 | N, S, J \rangle = BN(N+1) - DN^2(N+1)^2$$
$$- (1/3)[\lambda + \lambda_D N(N+1)][3X(X-1)$$
$$- 8N(N+1)]/[(2N-1)(2N+3)] - (1/2)\gamma X \qquad (3)$$

and

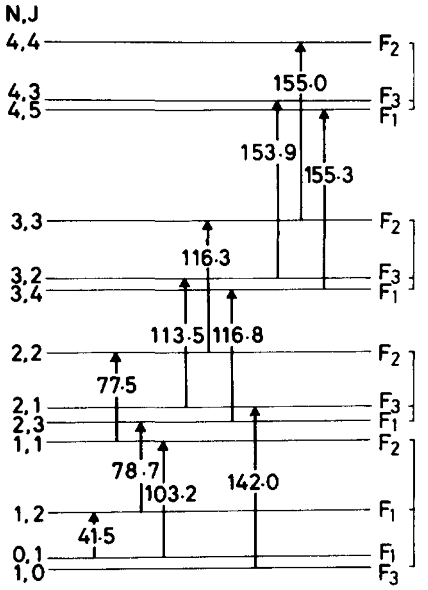

FIG. 2. The observed rotation/fine structure transitions of NCl.

$$\langle N+2,S,J|H_1|N,S,J\rangle = 2[\lambda+\lambda_D N(N+1)][(N+1)(N+2)]^{1/2}/(2N+3)\ , \tag{4}$$

where

$$X = N(N+1) - J(J+1) + 2\ . \tag{5}$$

The hyperfine Hamiltonian is expressed as follows:

$$H_{\mathrm{hfs}} = b(\mathrm{N})\mathbf{I}(\mathrm{N})\cdot\mathbf{S} + c(\mathrm{N})I_z(\mathrm{N})S_z + b(\mathrm{Cl})\mathbf{I}(\mathrm{Cl})\cdot\mathbf{S} + c(\mathrm{Cl})I_z(\mathrm{Cl})S_z + \mathrm{H_Q}(\mathrm{N}) + \mathrm{H_Q}(\mathrm{Cl}) + \mathrm{H_{nsr}}(\mathrm{Cl})\ , \tag{6}$$

where b(N), c(N), b(Cl), and c(Cl) denote the magnetic hyperfine coupling constants of the N and Cl nuclei defined by Frosch and Foley,[12] $\mathrm{H_Q}$(N) and $\mathrm{H_Q}$(Cl) the Hamiltonians, respectively, for the N and Cl nuclear quadrupole coupling effects, and $\mathrm{H_{nsr}}$(Cl) represents the Hamiltonian for the Cl nuclear spin/overall rotation interaction, simply given by $C_I(\mathrm{Cl})\mathbf{I}(\mathrm{Cl})\cdot\mathbf{N}$. The hyperfine matrix elements for a single nuclear spin interacting with the electron spin have been worked out, for example, by Brown *et al.*[13] using a Hund's case (b) representation and the spherical tensor formalism. Their reduced coefficients are related to b(Cl), c(Cl), and q(Cl) (the field gradient) as follows:

$$a_c = b(\mathrm{Cl}) + c(\mathrm{Cl})/3,\quad T_0^2(c) = c(\mathrm{Cl})/3\ ,\quad \text{and } T_0^2(\nabla E) = q(\mathrm{Cl})/2\ . \tag{7}$$

Brown *et al.* treatment can be extended to a two nuclear spin system by using the standard spherical tensor formalism.[14] The matrix elements of $\mathrm{H_{hfs}}$ for the second nucleus N are given by

$$\begin{aligned}
&\langle N',S,J',I_1,F_1',I_2,F,M_F|H_{\mathrm{hfs}}|N,S,J,I_1,F_1,I_2,F,M_F\rangle = \delta_{NN'}(-1)^{2F_1+F+2J'+S+N+I_1+I_2}\\
&\quad\times[(2F_1'+1)(2F_1+1)(2J'+1)(2J+1)S(S+1)(2S+1)I_2(I_2+1)(2I_2+1)]^{1/2}\\
&\quad\times\begin{Bmatrix}F & I_2 & F_1'\\ 1 & F_1 & I_2\end{Bmatrix}\begin{Bmatrix}I_1 & J' & F_1'\\ 1 & F_1 & J\end{Bmatrix}\begin{Bmatrix}N & J' & S\\ 1 & S & J\end{Bmatrix}[b(\mathrm{N})+c(\mathrm{N})/3]\\
&\quad+(-1)^{2F_1+F+J'+N'+I_1+I_2}(30)^{1/2}[(2F_1'+1)(2F_1+1)(2J'+1)(2J+1)\\
&\quad\times(2N'+1)(2N+1)S(S+1)(2S+1)I_2(I_2+1)(2I_2+1)]^{1/2}\\
&\quad\times\begin{Bmatrix}F & I_2 & F_1'\\ 1 & F_1 & I_2\end{Bmatrix}\begin{Bmatrix}I_1 & J' & F_1'\\ 1 & F_1 & J\end{Bmatrix}\begin{Bmatrix}N' & N & 2\\ S & S & 1\\ J' & J & 1\end{Bmatrix}\begin{pmatrix}N' & 2 & N\\ 0 & 0 & 0\end{pmatrix}[c(\mathrm{N})/3]+\begin{pmatrix}I_2 & 2 & I_2\\ -I_2 & 0 & I_2\end{pmatrix}^{-1}(-1)^{2F_1+I_2+F+J'+I_1+J+S}\\
&\quad\times[(2F'+1)(2F+1)(2J'+1)(2J+1)(2N'+1)(2N+1)]^{1/2}\\
&\quad\times\begin{Bmatrix}F & I_2 & F_1'\\ 2 & F_1 & I_2\end{Bmatrix}\begin{Bmatrix}I_1 & J' & F_1'\\ 2 & F_1 & J\end{Bmatrix}\begin{Bmatrix}N' & J' & S\\ J & N & 2\end{Bmatrix}\begin{pmatrix}N' & 2 & N\\ 0 & 0 & 0\end{pmatrix}[eQq(\mathrm{N})/4]\ .
\end{aligned}\tag{8}$$

The Hamiltonian matrix thus set up is obviously divided into blocks specified by the values of the total angular momentum quantum number F. Each block is further factored into two according to N even or odd. For example, the matrix with $F=3.5$ and $N=$ even has a dimension of 18×18. In each block the diagonal terms with the same N and same J values are nearly degenerate. The dimension of such degenerate subblock is less than 4, because $I(\mathrm{Cl}) = 1.5$ and $I(\mathrm{N}) = 1.0$. In the $F=3.5$ matrix, e.g., the $N=2$, $J=3$ subblock is 3×3, according to three possible values of $F_1 = 2.5$, 3.5, and 4.5. When the matrix is numerically diagonalized, levels within a subblock are severely mixed by the hyperfine interaction so that it is no longer possible to correlate an eigenstate with a value of F_1. Therefore, an index ν is assigned to each eigenstate in the N, J, F subblock such that $\nu=1$, 2, and 3 correspond to the lowest, middle, and highest levels. (For some subblocks only $\nu=1$ or $\nu=1$ and 2 levels are present.) The $N=2$, $J=3$, $F=3.5$, $\nu=1$ level is, for example, expressed in terms of the basis functions $|F_1\rangle$ as

$$|\nu=1\rangle = 0.33\,|F_1=2.5\rangle + 0.78\,|F_1=3.5\rangle + 0.50\,|F_1=4.5\rangle\ . \tag{9}$$

The relative intensity of the transition was calculated from the squared dipole moment matrix element summed over all directions in space and also all M_F values. When the original basis set is used, the matrix element is given by

$$\begin{aligned}
&\langle N',S,J',I_1,F_1',I_2,F',M_F'|\mu_Z|N,S,J,I_1,F_1,I_2,F,M_F\rangle = \begin{pmatrix}F_1 & 1 & F\\ -M_F & 0 & M_F\end{pmatrix}(-1)^{F_1'+F+I_2+J'+F_1+I_1+N'+J}\\
&\quad\times[(2F'+1)(2F+1)(2F_1'+1)(2F_1+1)(2J'+1)(2J+1)(2N'+1)(2N+1)]^{1/2}\\
&\quad\times\begin{Bmatrix}I_2 & F_1' & F'\\ 1 & F & F_1\end{Bmatrix}\begin{Bmatrix}I_1 & J' & F_1'\\ 1 & F_1 & J\end{Bmatrix}\begin{Bmatrix}N' & J' & S\\ J & N & 1\end{Bmatrix}\begin{pmatrix}N' & 1 & N\\ 0 & 0 & 0\end{pmatrix}\mu\ .
\end{aligned}\tag{10}$$

Since F_1 is not a good quantum number, Eq. (10) needs to be transformed to the matrix element in the eigenstate basis. The relative intensities thus calculated were plotted against the frequency to readily be compared with the observed spectra.

TABLE I. Observed rotational transitions of the N ^{35}Cl radical (MHz).

N'	J'	F'	ν'	N''	J''	F''	ν''	Obs.	o−c	wt.
1	2	2.5	3	0	1	1.5	3	41 515.597	0.052	1.0
1	2	2.5	2	0	1	1.5	2	41 517.701	−0.028	1.0
1	2	3.5	2	0	1	2.5	2	41 520.087	−0.019	1.0
1	2	4.5	1	0	1	3.5	1	41 527.777	−0.028	1.0
1	2	3.5	1	0	1	2.5	1	41 533.011	−0.040	1.0
2	2	3.5	2	1	1	2.5	2	77 503.976	0.007	1.0
2	2	2.5	2	1	1	1.5	2	77 509.899	0.011	1.0
2	2	2.5	3	1	1	2.5	2	77 525.037	0.001	1.0
2	2	2.5	1	1	1	1.5	1	77 538.985	0.014	1.0
2	2	3.5	1	1	1	2.5	1	77 542.546	0.006	1.0
2	2	4.5	1	1	1	3.5	1	77 547.347	0.010	1.0
2	3	4.5	1	1	2	4.5	1	78 639.127	−0.001	1.0
2	3	3.5	1	1	2	3.5	1	78 656.223	−0.016	1.0
2	3	2.5	1	1	2	2.5	1	78 669.215	−0.047	1.0
2	3	1.5	1	1	2	1.5	1	78 681.536	−0.014	1.0
2	3	2.5	3	1	2	1.5	3	78 687.491	−0.026	1.0
2	3	3.5	3	1	2	2.5	3	78 688.055	−0.007	1.0
2	3	2.5	2	1	2	1.5	2	78 688.659	0.066	1.0
2	3	3.5	2	1	2	2.5	2	78 689.423	−0.026	1.0
2	3	4.5	2	1	2	3.5	2	78 690.095	0.013	1.0
2	3	2.5	1	1	2	1.5	1	78 690.095	−0.167	0.1
2	3	5.5	1	1	2	4.5	1	78 693.975	−0.003	1.0
2	3	3.5	1	1	2	2.5	1	78 695.945	−0.007	1.0
2	3	4.5	1	1	2	3.5	1	78 697.500	−0.002	1.0
1	1	3.5	1	0	1	3.5	1	103 157.401	−0.014	1.0
1	1	2.5	1	0	1	2.5	2	103 186.756	−0.008	1.0
1	1	3.5	1	0	1	2.5	1	103 221.038	0.003	1.0
1	1	1.5	2	0	1	2.5	2	103 233.398	−0.023	1.0
1	1	1.5	1	0	1	1.5	2	103 237.136	−0.013	1.0
1	1	1.5	3	0	1	2.5	1	103 304.327	−0.013	1.0
1	1	2.5	2	0	1	1.5	1	103 312.045	0.014	1.0
3	2	2.5	3	2	1	1.5	3	113 492.714	−0.010	1.0
3	2	3.5	2	2	1	2.5	2	113 512.326	0.002	1.0
3	2	1.5	2	2	1	0.5	2	113 521.989	0.001	1.0
3	2	1.5	3	2	1	1.5	3	113 534.620	−0.014	1.0
3	2	2.5	2	2	1	1.5	2	113 535.297	0.012	1.0
3	2	1.5	1	2	1	0.5	1	113 541.266	0.008	1.0
3	2	2.5	1	2	1	1.5	1	113 544.455	0.004	1.0
3	2	0.5	1	2	1	0.5	2	113 545.464	0.053	1.0
3	2	3.5	1	2	1	2.5	1	113 546.571	0.011	1.0
3	2	4.5	1	2	1	3.5	1	113 552.277	0.008	1.0
3	2	0.5	2	2	1	1.5	3	113 562.450	−0.027	1.0
3	2	2.5	3	2	1	2.5	2	113 563.730	0.025	1.0
3	2	1.5	2	2	1	1.5	2	113 564.436	0.034	1.0
3	2	1.5	3	2	1	2.5	2	113 605.613	−0.003	1.0
3	2	2.5	2	2	1	2.5	1	113 608.381	−0.009	1.0
3	2	3.5	2	2	1	3.5	1	113 618.079	−0.001	1.0
3	3	1.5	2	2	2	0.5	2	116 283.359	−0.083	1.0
3	3	3.5	3	2	2	2.5	3	116 284.050	0.039	1.0
3	3	1.5	1	2	2	0.5	1	116 284.050	−0.110	0.1
3	3	2.5	3	2	2	1.5	3	116 285.160	0.084	0.7
3	3	2.5	2	2	2	1.5	2	116 285.160	−0.058	0.7
3	3	0.5	1	2	2	0.5	2	116 286.564	−0.041	1.0
3	3	4.5	1	2	2	3.5	2	116 287.821	0.072	0.5
3	3	3.5	1	2	2	2.5	2	116 287.821	−0.166	0.3
3	3	2.5	1	2	2	1.5	1	116 288.244	−0.021	1.0
3	3	1.5	1	2	2	1.5	2	116 288.898	0.095	0.7
3	3	2.5	2	2	2	2.5	3	116 288.898	−0.010	0.7
3	3	1.5	2	2	2	1.5	3	116 291.429	−0.014	1.0
3	3	3.5	2	2	2	2.5	2	116 292.457	0.014	1.0
3	3	4.5	2	2	2	3.5	2	116 293.613	0.005	1.0
3	3	3.5	1	2	2	2.5	1	116 295.382	0.000	1.0
3	3	4.5	1	2	2	3.5	1	116 296.541	−0.006	1.0
3	3	3.5	2	2	2	2.5	1	116 299.838	−0.001	1.0
3	3	5.5	1	2	2	4.5	1	116 302.263	0.036	1.0
3	3	4.5	2	2	2	3.5	1	116 302.263	−0.143	0.1
3	4	5.5	1	2	3	5.5	1	116 815.278	−0.010	1.0

TABLE I (*Continued*).

N'	J'	F'	v'	N''	J''	F''	v''	Obs.	o−c	wt.
3	4	4.5	1	2	3	4.5	1	116 828.269	−0.020	1.0
3	4	3.5	1	2	3	3.5	1	116 839.767	−0.009	1.0
3	4	2.5	1	2	3	2.5	1	116 854.543	−0.002	1.0
3	4	1.5	1	2	3	0.5	1	116 862.213	0.051	1.0
3	4	2.5	1	2	3	1.5	1	116 863.183	−0.075	1.0
3	4	3.5	3	2	3	2.5	3	116 863.814	−0.006	1.0
3	4	4.5	3	2	3	3.5	3	116 864.393	0.005	1.0
3	4	2.5	2	2	3	1.5	2	116 864.393	0.009	0.1
3	4	3.5	2	2	3	2.5	2	116 864.737	0.004	1.0
3	4	4.5	2	2	3	3.5	2	116 865.209	0.023	1.0
3	4	5.5	2	2	3	4.5	2	116 865.498	0.008	1.0
3	4	3.5	1	2	3	2.5	1	116 866.468	0.002	1.0
3	4	6.5	1	2	3	5.5	1	116 867.795	0.007	1.0
3	4	4.5	1	2	3	3.5	1	116 869.538	−0.014	1.0
3	4	5.5	1	2	3	4.5	1	116 870.151	0.014	1.0
2	1	3.5	1	1	0	2.5	1	141 926.830	0.018	1.0
2	1	2.5	1	1	0	1.5	1	141 957.658	0.016	1.0
2	1	1.5	1	1	0	0.5	1	141 988.570	0.016	1.0
2	1	0.5	1	1	0	0.5	1	142 022.821	0.013	1.0
2	1	1.5	2	1	0	1.5	1	142 030.748	0.001	1.0
2	1	2.5	2	1	0	2.5	1	142 032.571	0.004	1.0
2	1	0.5	2	1	0	1.5	1	142 073.160	−0.002	1.0
2	1	1.5	3	1	0	2.5	1	142 103.551	0.002	1.0
4	3	2.5	3	3	2	1.5	3	153 877.686	−0.008	1.0
4	3	1.5	2	3	2	0.5	2	153 880.947	−0.001	1.0
4	3	3.5	3	3	2	2.5	3	153 885.517	−0.012	1.0
4	3	2.5	2	3	2	1.5	2	153 892.603	−0.004	1.0
4	3	4.5	2	3	2	3.5	2	153 894.131	−0.011	1.0
4	3	1.5	1	3	2	0.5	1	153 895.424	−0.033	1.0
4	3	3.5	2	3	2	2.5	2	153 896.297	−0.003	1.0
4	3	3.5	1	3	2	2.5	1	153 897.613	−0.029	1.0
4	3	4.5	1	3	2	3.5	1	153 898.368	−0.014	1.0
4	3	2.5	1	3	2	1.5	1	153 899.048	0.025	1.0
4	3	0.5	1	3	2	0.5	2	153 900.887	−0.002	1.0
4	3	5.5	1	3	2	4.5	1	153 903.209	−0.012	1.0
4	3	1.5	2	3	2	1.5	3	153 908.777	−0.014	1.0
4	3	2.5	3	3	2	2.5	3	153 919.603	−0.001	1.0
4	3	3.5	3	3	2	3.5	2	153 936.885	−0.025	1.0
4	3	4.5	2	3	2	4.5	1	153 959.934	−0.018	1.0
4	4	3.5	2	3	3	2.5	2	155 049.071	−0.012	1.0
4	4	4.5	3	3	3	3.5	3	155 049.565	0.002	1.0
4	4	3.5	3	3	3	2.5	3	155 049.858	0.006	1.0
4	4	3.5	1	3	3	2.5	1	155 051.543	−0.010	1.0
4	4	4.5	1	3	3	3.5	1	155 052.864	−0.002	1.0
4	4	5.5	1	3	3	4.5	1	155 053.750	0.012	1.0
4	4	4.5	2	3	3	3.5	2	155 055.920	−0.005	1.0
4	4	5.5	2	3	3	4.5	2	155 056.831	0.010	1.0
4	4	6.5	1	3	3	5.5	1	155 058.605	0.013	1.0
4	5	6.5	1	3	4	6.5	1	155 298.904	0.006	1.0
4	5	5.5	1	3	4	5.5	1	155 309.253	0.001	1.0
4	5	4.5	1	3	4	4.5	1	155 319.363	0.017	1.0
4	5	3.5	1	3	4	3.5	1	155 335.145	0.025	1.0
4	5	2.5	1	3	4	1.5	1	155 346.117	−0.001	1.0
4	5	4.5	3	3	4	3.5	3	155 347.054	−0.021	0.5
4	5	3.5	1	3	4	2.5	1	155 347.054	0.014	0.5
4	5	5.5	3	3	4	4.5	3	155 347.587	0.010	1.0
4	5	3.5	2	3	4	2.5	2	155 347.587	0.143	0.4
4	5	6.5	2	3	4	5.5	2	155 348.202	−0.051	1.0
4	5	4.5	1	3	4	3.5	1	155 349.115	−0.008	1.0
4	5	7.5	1	3	4	6.5	1	155 349.792	0.038	1.0
4	5	5.5	1	3	4	4.5	1	155 351.130	0.030	1.0
4	5	6.5	1	3	4	5.5	1	155 351.404	0.007	1.0

ANALYSIS

The hyperfine coupling constants were first estimated by referring to those of the related molecules. The nitrogen b(N) and c(N) constants of NH, NO, and NS are not much different one another, as shown below, and some averages of them were used as initial values. For the Cl atom the averages of the CCl and OCl hyperfine constants were employed. These trial values gave calculated spectra very similar in pattern to the observed, allowing to readily make an assignment. In fact, these initial values were later found to be very close to the final values of the hyperfine coupling constants. Table I lists the observed frequencies with the assignment. By iterative least-squares fitting, we obtained a set of molecular constants, as shown in Table II. In the least-squares fit, unresolved hyperfine components were weighted in such a way that the weight of each component was proportional to the squared relative intensity and the sum of the weights over unresolved components was normalized to the unity. The standard error of the fit is 29 kHz, which is nearly equal to the experimental error. It is to be noted that the Cl nuclear spin rotation interaction was found to make a significant contribution to the observed spectra.

DISCUSSION

As shown in Table II, the molecular constants of Colin and Jones[9] differ from the present results by more than their experimental errors. However, it must be noted that they employed Schlapp's formula[15] in analyzing their spectra, which has been shown to be insufficient in fitting spectral lines to an accuracy better than 1 MHz.[16] We have thus reanalyzed their ground-state combination differences using our computer program and have obtained molecular constants that agree with ours within experimental uncertainties of Ref. 9. Therefore, the discrepancies are completely removed. The sign ambiguity for the λ constant mentioned in Ref. 9 has also been eliminated by the present work; the choice of Colin and Jones was supported.

Using our molecular constants and the energy level expressions [Eqs. (3)-(5)] for the ground state, the observed transitions reported in Ref. 9 were reanalyzed to obtain excited state parameters. The fitting was made with the standard error of 0.018 cm^{-1} and resulted in the molecular constants that were considerably different from those of Ref. 9, as shown in Table III.

TABLE II. Molecular constants of N^{35}Cl (MHz).[a]

	This work	Colin and Jones[b]
B	19383.4655(42)	19392
D	0.04795(16)	0.0534
λ	56390.850(16)	53243
λ_D	−0.2568(29)	···
γ	−208.6306(96)	−214.4

Hyperfine coupling constants (present work)

b(Cl)	22.774(29)	b(N)	44.011(33)
c(Cl)	−57.764(36)	c(N)	−63.159(51)
eQq(Cl)	−63.13(18)	eQq(N)	1.842(96)
C_I(Cl)	0.0152(60)		

[a] Values in parentheses denote three standard deviations.

[b] Reference 9. The values were converted from cm^{-1} to MHz by using $c = 29\,979.2458$ MHz/cm^{-1}. Note that these values were obtained using Schlapp's formula; see the text.

TABLE III. Molecular constants of N^{35}Cl in the $b\,^1\Sigma^+$ state (cm^{-1}).[a]

	This work	Colin and Jones[b]
B'	0.682567(51)	0.68284
D'	0.000001476(48)	0.00000165
ν_{00}	15040.088(11)	15038.94

[a] Values in parentheses denote three standard deviations.

[b] From Ref. 9.

The NCl molecule is the first diatomic free radical investigated by microwave spectroscopy which consists of nuclei both having nonzero nuclear spins. The b and c magnetic and the eQq electrostatic hyperfine coupling constants which were determined for both atoms in the molecule were used in elucidating the electronic structure of the molecule.

The electron configuration of NCl in the ground electronic state is expressed as $KKL(5\sigma)^2(6\sigma)^2(2\pi)^4(7\sigma)^2(3\pi)^2$, and the two unpaired electrons occupy the 3π orbital. The Fermi contact term a_C calculated from $b+c/3$ is 22.958 and 3.519 MHz, respectively, for the N and Cl atoms, which lead, when compared with the atomic values of 1811 and 5723 MHz,[17] to the s character of 1.27% and 0.06%, respectively.

Although the d constant is not available, the $g_S\beta g_N\beta_N \times\langle 1/r^3\rangle_s$ value may be calculated from the c constant by assuming that the angular part $3\cos^2\theta-1$ can be evaluated with the hydrogenic p_π wave function, namely,

$$g_S\beta g_N\beta_N\langle 1/r^3\rangle_S=-(5/3)c\ . \qquad (11)$$

The observed c constants give $g_S\beta g_N\beta_N\langle 1/r^3\rangle_s$ to be 105.265 and 96.273 MHz, respectively, for the N and Cl atoms, and a comparison of these values with the atomic values, 138.8 and 439.0 MHz,[17] yields the spin density to be 75.8% and 21.9%, respectively, for N and Cl.

TABLE IV. Hyperfine coupling constants of three diatomic chlorides (MHz).

Molecule	n[a]	b	c	Spin density on the Cl atom(%)
CCl[b]	1	12.0(15)	−39.5(16)	15.7[d]
NCl	2	22.774(29)	−57.764(36)	21.9
OCl[c]	3	45.0(67)	−92.4(67)	32.4[d]

[a] The number of the electrons in the 3π orbital.

[b] From Ref. 18.

[c] From Ref. 20.

[d] Calculated from $d+c/3$.

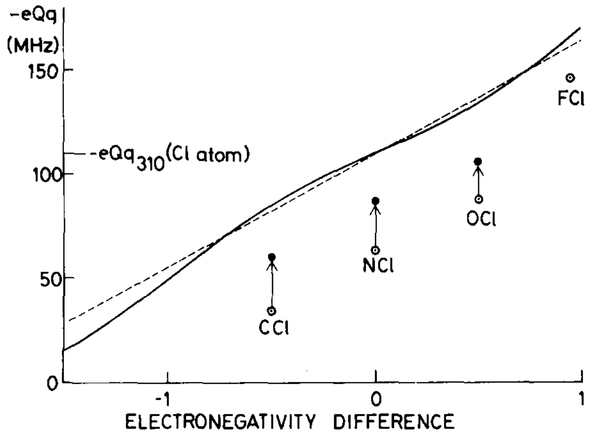

FIG. 3. The nuclear quadrupole coupling constants observed for second-row element chlorides vs the electronegativity difference. The observed constants are indicated by open circles, whereas the corrected values are shown by closed circles; the arrows designate the corrections for back donations (see the text). The solid curve was calculated from a formula proposed by Gordy and Cook (Ref. 24).

When the spin density on the Cl atom is designated by ρ, the number of electrons occupying the 3π and 2π orbitals around the Cl atom is approximately given, respectively, by $n\rho$ and $4(1-\rho)$, because the 3π and 2π orbitals are orthogonal to each other.[18] Here n denotes the number of π electrons in the 3π orbital, which is 2 for NCl. The amount of the p_π electrons transferred from Cl to N is thus given by

$$\Delta_p = 4 - [n\rho + 4(1-\rho)] = (4-n)\rho \ , \tag{12}$$

which is 0.44 for NCl.

Table IV shows that the b and c constants of Cl in three diatomic chlorides change smoothly with the number of 3π electrons n. This fact explains that the initial estimates of the Cl hyperfine constants are close to the observed. The electron transfer Δ_p from Cl to C or O is calculated to be 0.47 and 0.32 in CCl and OCl, respectively, which are compared with 0.44 in NCl.[19] A similar comparison is made in Table V for four diatomic nitrides. Here the b(N) and c(N) constants are not much different for the first three molecules. The initial estimates, $b(\mathrm{N}) \sim 41$ MHz and $c(\mathrm{N}) \sim -60$ MHz, for NC turned out to be close to the final values. The spin density seems to reflect the effect of back donation, because it increases with the electronegativity difference.

TABLE V. Hyperfine coupling constants of four diatomic nitrides (MHz).

Molecule	b	c	Spin density on the N atom(%)
NH[a]	41.86(99)	−67.94(183)	81.6[d]
NO[b]	41.79(15)	−58.66(15)	67.0[e]
NS[c]	36.3(111)	−46.8(111)	51.4[e]
NCl	44.011(33)	−63.159(51)	75.8[d]

[a] From Ref. 5.
[b] From Ref. 21.
[c] From Ref. 22.
[d] The spin density is calculated from c.
[e] The spin density is calculated from $d+c/3$.

TABLE VI. Chlorine nuclear quadrupole coupling constant of XCl (MHz).

X	n[a]	eQq	$eQq^{\mathrm{corr}\,c}$
C	1	−34.26(16)	−60.10
N	2	−63.13(18)	−87.16
O	3	−87.95(23)	−105.73
F[b]	4	−145.871	

[a] The number of the electrons in the 3π orbital.
[b] From Ref. 23.
[c] Corrected for back donation (see the text).

Another interesting comparison is made in Table VI on the values of eQq(Cl) of four diatomic chloride molecules which have $n=1$–4 electrons in the 3π orbital. The value of $-eQq$ again increases smoothly with n. This fact has allowed us to estimate eQq in NCl. As briefly discussed in a previous paper,[18] the values of eQq can be explained by the electronegativity difference and the π electron delocalization (or back donation). Since an electron in a π orbital contributes $(-1/2)(eQq)_{310}$ to the coupling constant, $-(\Delta_p/2)(eQq)_{310}$ must be added to the observed eQq value before it is employed to estimate the ionic character of the σ bond. The corrected values of eQq are also included in Table VI and are plotted in Fig. 3 against the electronegativity difference. Gordy and Cook[24] have pointed out that the ionic character i_c of a σ bond estimated from the corrected eQq using the relation:

$$i_c = 1 + eQq/(eQq)_{310} \ , \tag{13}$$

is approximately proportional to the electronegativity difference, as indicated by a broken line in Fig. 3. The data listed in Table VI do not fall on the broken line, but on a curve slightly shifted from the broken line.

The Cl nuclear spin-rotation interaction may be estimated using an approximate formula given in a previous paper[25]:

$$|C_I/\gamma| = |a/A_{\mathrm{SO}}| \ . \tag{14}$$

The effective value of the spin-orbit coupling constant A_{SO} was estimated from the atomic values (76 and 586 cm^{-1}, respectively, for N and Cl)[26] weighted by the spin densities, 75.8% and 21.9% for the two atoms, namely $A_{\mathrm{SO}} = 190$ cm^{-1}. By inserting this A_{SO} value, the atomic value of $a = 439$ MHz,[17] and the spin-rotation interaction constant γ determined in the present work in Eq. (14), C_I was calculated to be 16.1 kHz, which may be compared with the observed values, 15.2 kHz.

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