Microwave Spectroscopy of Boron Chloride (BCl). The Chlorine Nuclear Quadrupole Coupling Constant

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The pure rotational spectrum of an unstable diatomic molecule, boron chloride (BCl), has been observed in the millimeter wave region. The BCl molecule was directly generated in a 3.7-m long free space absorption cell by a d.c. glow discharge in BCl_3. Rotational transitions of $^{11}B^{35}Cl$ and $^{11}B^{37}Cl$ in the ground vibrational state, which are split into a few components by the nuclear electric quadrupole interactions, have been observed and analyzed to yield molecular constants including the chlorine nuclear quadrupole coupling constant with high accuracy. The eQq constant thus determined is discussed along with those of other diatomic chlorides, to obtain information on the electronic structure of the molecules.

The chlorine nuclear quadrupole coupling constant [eQq(Cl)] has been determined in a number of molecules in the gas phase by means of microwave spectroscopy, and its significance for the electronic structure of the molecules has been explored in detail.[1] Thanks to recent developments in microwave spectroscopic techniques, several unstable molecules containing a chlorine nucleus have also been investigated; OCl,[2,3] CCl,[4] ClBO,[5] and NCl[6] are such examples. A diatomic molecule consisting of a second row element and a chlorine atom has the electron configuration in the ground state expressed as $KKL(5\sigma)^2(6\sigma)^2(2\pi)^4(7\sigma)^2(3\pi)^n$, where $n=1,2,3$, and 4 apply to CCl, NCl, OCl, and FCl.[7] As has been shown previously,[6] the eQq(Cl) constants of the molecules with $n=1$—4 fall on a smooth curve when they are plotted against n, the number of electrons in the 3π (HOMO) orbital, provided that the observed values of eQq for CCl, NCl, and OCl were corrected for π-electron back donation, as estimated from the magnetic hyperfine coupling constants. It is interesting to see whether the eQq(Cl) constant of BCl conforms with the prediction from those of other molecules; BCl is the first member with $n=0$ of this series.

The ground-state rotational and vibrational constants of BCl were first obtained by Herzberg and Hushley[8] from the analysis of the observed ultraviolet spectrum. Maki *et al.*[9] have recently observed vibration-rotation spectra of BCl by infrared diode laser spectroscopy in the 12-μm region. They generated BCl in the optical path by means of either a dc glow discharge or a 2450 MHz microwave discharge in BCl_3. They improved the accuracy of the ground-state constants over that of the previous study, but were unable to resolve the hyperfine structure. They have attempted to observe the pure rotational spectrum at around 80 GHz with a Stark-modulated microwave spectrometer without success.[9]

The present paper reports the observation of the rotational transitions of BCl and precise ground-state constants including eQq(Cl) obtained therefrom.

Experimental

The microwave spectrometer employed in the present study is a source modulation spectrometer with a free space absorption cell of 3.7-m length sealed with Teflon lenses at both ends.[10] The BCl molecule was generated directly in the cell by a dc glow discharge in BCl_3; BCl_3 was pumped continuously through the cell by a mechanical booster pump of 67 l s^{-1}. The optimum pressure for BCl_3 in the cell was about 20 mTorr (2.7 Pa) as measured by an uncalibrated Pirani gauge. The dc discharge current of 100 mA was required to obtain the S/N ratio sufficient for the measurement. We have also attempted to observe BCl lines using a 1-m long cell, where BCl was generated by a microwave discharge in BCl_3 in a side arm used as the inlet; the discharge products were rapidly pumped through the cell. Although the sample pressure (5 to 30 mTorr or 0.7 to 4.0 Pa) and the discharge current were carefully adjusted, we were unable to observe the BCl spectrum by this arrangement. This result indicates that BCl is short-lived and exists only in and near the discharged region.

Using the molecular constants of Maki *et al.*,[9] the frequency of the $J=4\leftarrow3$ transition of $^{11}B^{35}Cl$ was calculated to be about 163.3 GHz, and searching for this species was initiated in this region. A fairly strong absorption line with resolved hyperfine structure was observed at 13 MHz higher than that predicted for $J=4\leftarrow3$; its trace is shown in Fig. 1. It vanished immediately when the discharge was turned off, and was thus ascribed to a species of short life. Both the observed hyperfine structure and the short lifetime of the species indicated that the observed line is due to BCl. This assignment was confirmed by observing the corresponding transition of $^{11}B^{37}Cl$ and also the next lowest transition, $J=3\leftarrow2$. The $J=2\leftarrow1$ transition was found to be complicated because of additional splittings due to the ^{11}B nuclear quadrupole interaction, as exemplified by the trace shown in Fig. 2 (see also Table 1). The lowest $J=1\leftarrow0$ transition was also observed, but was too weak to measure the hyperfine components accurately.

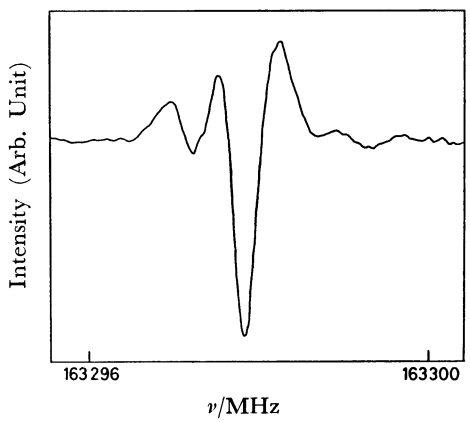

Fig. 1. The $J=4\leftarrow3$ transition of $^{11}B^{35}Cl$.

TABLE 1. OBSERVED ROTATIONAL TRANSITION FREQUENCIES OF $^{11}B^{35}Cl$

$J \leftarrow J'$	$F_1' \leftarrow F_1$	$F' \leftarrow F$	$\frac{\nu_{obsd}}{MHz}$	$\frac{\nu_{obsd} - \nu_{calcd}}{MHz}$	Weight[a]
4←3	5.5←4.5	7←6	163 297.841	−0.002	0.035
		6←5		0.039	0.024
		5←4		0.075	0.016
		4←3		0.046	0.011
	4.5←3.5	6←5		−0.043	0.022
		5←4		0.082	0.014
		4←3		0.081	0.008
		3←2		−0.010	0.005
	3.5←2.5	4←3	163 297.234	0.012	0.113
		3←2		−0.022	0.057
	2.5←1.5	3←2		−0.003	0.054
		2←1		0.161	0.017
		1←0		−0.016	0.004
	4.5←4.5	6←6	163 293.573	0.000	1.000
	3.5←3.5	4←4	163 299.318	0.035	0.173
		5←5		−0.048	0.341
3←2	4.5←3.5	6←5	122 478.069	0.015	0.042
		5←4		0.093	0.026
		4←3		0.168	0.016
		3←2		0.094	0.010
	3.5←2.5	5←4		−0.063	0.022
		4←3		0.231	0.012
		3←2		0.127	0.006
		2←1		−0.084	0.003
	2.5←1.5	4←3	122 477.157	−0.001	0.123
		2←2		0.147	0.005
		2←1		0.147	0.015
		1←1		−0.174	0.003
		1←0		−0.174	0.003
	1.5←0.5	3←2		0.041	0.065
		1←1		0.073	0.008
	2.5←2.5	4←4	122 479.998	−0.089	0.261
		3←3		0.099	0.094
		2←2		−0.131	0.033
	1.5←1.5	3←3	122 481.348	0.019	1.000
2←1	3.5←2.5	5←4	81 654.517	0.041	0.082
		4←3		0.219	0.044
		3←3		−0.098	0.001
		3←2		0.105	0.022
		2←1		0.061	0.011
	2.5←1.5	4←3		−0.136	0.027
		2←1		0.010	0.003
	2.5←2.5	3←3	81 650.245	−0.067	0.391
		2←2		0.009	0.140
	2.5←2.5	1←1	81 649.812	−0.006	0.009
	1.5←0.5	3←2		0.085	0.191
		2←2		0.085	0.024
		2←1		−0.001	0.024
		1←1		−0.001	0.024
	3.5←2.5	4←4	81 653.804	0.048	0.006
	2.5←1.5	3←2		0.063	0.101
		2←2		−0.065	0.010
	0.5←0.5	2←2		−0.136	0.028
		2←1		−0.222	0.028
		1←2		−0.194	0.028
	1.5←1.5	3←3	81 657.597	0.014	0.424
		2←3		0.014	0.026
		2←1		−0.029	0.035
	1.5←1.5	3←2	81 656.947	−0.041	0.078
		2←2		−0.041	0.160
		1←2		−0.041	0.102

a) The weight for unresolved components is taken to be proportional to the square of the calculated relative intensity.

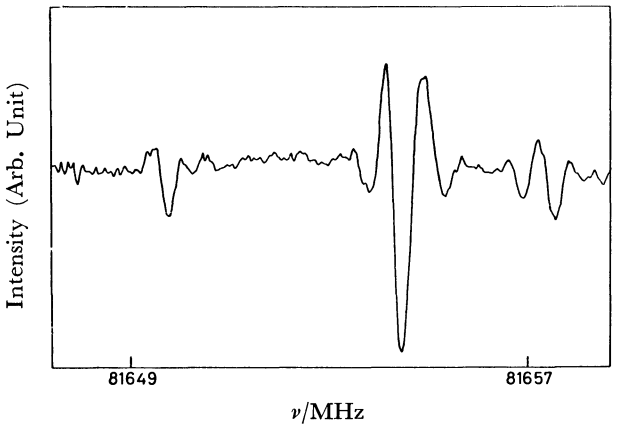

Fig. 2. The $J=2\leftarrow1$ transition of $^{11}B^{35}Cl$. The spectrum was synthesized from a few consecutive scans, each covering a region of 4 MHz.

The observed frequencies are listed in Table 1 with the assignment; each frequency was determined by taking the average of three up-sweep and three down-sweep measurements. A smaller number of lines were observed for $^{11}B^{37}Cl$ than for $^{11}B^{35}Cl$, because of poorer S/N ratio. The frequencies observed for $^{11}B^{37}Cl$ are given in Table 2. The standard deviation of the frequency measurement is less than 20 kHz except for a few weak lines.

Analysis of the Observed Spectrum

Because both nuclei in the BCl molecule show the quadrupole coupling interaction, a coupling scheme of the angular momenta, $\mathbf{F}_1=\mathbf{J}+\mathbf{I}(\mathrm{Cl})$ and $\mathbf{F}=\mathbf{F}_1+\mathbf{I}(^{11}\mathrm{B})$, was employed to analyze the hyperfine structure, where $\mathbf{J}$, $\mathbf{I}(\mathrm{Cl})$, and $\mathbf{I}(^{11}\mathrm{B})$ denote the rotational, Cl nuclear spin, and ^{11}B nuclear spin angular momenta, respectively; both $I(^{35,37}\mathrm{Cl})$ and $I(^{11}\mathrm{B})$ are 3/2. The $\Delta J=0$ matrix elements for the quadrupole coupling Hamiltonians, $\mathbf{H}_Q(\mathrm{Cl})$ and $\mathbf{H}_Q(\mathrm{B})$, are given by

$$\begin{aligned}&\langle I(\mathrm{Cl})JF_1'I(\mathrm{B})F'M_{F'}|\mathbf{H}_Q(\mathrm{Cl})|I(\mathrm{Cl})JF_1I(\mathrm{B})FM_F\rangle\\&=-\frac{1}{8}\delta_{F_1'F_1}\delta_{F'F}\delta_{M_{F'}M_F}\\&\times\frac{3C(C-1)-4J(J+1)I(\mathrm{Cl})[I(\mathrm{Cl})+1]}{(2J-1)(2J+3)I(\mathrm{Cl})[2I(\mathrm{Cl})-1]}eQq(\mathrm{Cl}),\end{aligned}\tag{1}$$

and

$$\begin{aligned}&\langle I(\mathrm{Cl})JF_1'I(\mathrm{B})F'M_{F'}|\mathbf{H}_Q(\mathrm{B})|I(\mathrm{Cl})JF_1I(\mathrm{B})FM_F\rangle\\&=-\delta_{F'F}\delta_{M_{F'}M_F}(-1)^{J+I(\mathrm{Cl})+F_1}[(2F_1+1)(2F_1'+1)]^{1/2}\\&\times\begin{Bmatrix}J & F_1 & I(\mathrm{Cl})\\ F_1' & J & 2\end{Bmatrix}(-1)^{I(\mathrm{B})+F_1+F}\\&\times\begin{Bmatrix}I(\mathrm{B}) & F_1 & F\\ F_1' & I(\mathrm{B}) & 2\end{Bmatrix}\left[\frac{J(J+1)(2J+1)}{(2J-1)(2J+3)}\right]^{1/2}\\&\times\left[\frac{[I(\mathrm{B})+1][2I(\mathrm{B})+1][2I(\mathrm{B})+3]}{I(\mathrm{B})[2I(\mathrm{B})-1]}\right]^{1/2}eQq(\mathrm{B})/4,\end{aligned}\tag{2}$$

where $C=J(J+1)+I(\mathrm{Cl})[I(\mathrm{Cl})+1]-F_1(F_1+1)$ and δ_{ij} and $\{\cdots\}$ denote Kronecker's delta and the Wigner 6j symbol, respectively. The matrix elements off-diagonal in J were ignored, since their contributions

Table 2. Observed rotational transition frequencies of $^{11}B^{37}Cl$

$J'\leftarrow J$	$F_1'\leftarrow F_1$	$F'\leftarrow F$	ν_{obsd} / MHz	$\nu_{obsd}-\nu_{calcd}$ / MHz	Weight[a]
4←3	5.5←4.5	7←6	161 191.074	−0.016	0.035
		6←5		0.027	0.024
		5←4		0.062	0.016
		4←3		0.035	0.011
	4.5←3.5	6←5		−0.059	0.022
		5←4		0.065	0.014
		4←3		0.062	0.008
		3←2		−0.011	0.005
3←2	4.5←3.5	6←5	120 879.834	−0.030	0.042
		5←4		0.052	0.026
		4←3		0.134	0.016
		3←2		0.058	0.010
	3.5←2.5	5←4		−0.111	0.022
		4←3		0.183	0.012
		3←2		0.074	0.006
		2←1		−0.115	0.003
	2.5←1.5	4←3	120 897.135	−0.059	0.123
		2←2		0.067	0.005
		2←1		0.067	0.015
		1←1		−0.212	0.003
		1←0		−0.212	0.003
	1.5←0.5	3←2		−0.009	0.065
		1←1		0.032	0.008
2←1	3.5←2.5	5←4	80 600.921	0.003	0.082
		4←3		0.183	0.044
		3←3		−0.136	0.001
		3←2		0.036	0.022
		2←1		0.018	0.011
	2.5←1.5	4←3		−0.178	0.027
		2←1		−0.029	0.003

a) See note a) of Table 1.

Table 3. Molecular constants of BCl[a)]

	$^{11}B^{35}Cl$	
	Present	Ref. 9[b)]
B_0/MHz	20 413.942 2(91)	20 412.40(93)
D_0/MHz	0.054 10(35)	0.055 10(157)
eQq(Cl)/MHz	−16.737(11)	
eQq(B)/MHz	−3.70[c)]	
	$^{11}B^{37}Cl$	
	Present	Ref. 9
B_0/MHz	20 150.562 0(182)	20 148.99
D_0/MHz	0.052 87(79)	0.053 68
eQq(Cl)/MHz	−13.191[d)]	
eQq(B)/MHz	−3.70[d)]	

a) Values in parentheses denote 2.5 times the standard deviations of the fit. b) Converted from the Dunham coefficients of Ref. 9. c) Determined from a lineshape simulation. d) Assumed. Calculated from $eQq(^{35}Cl)$.

were found to be small. All other $\Delta J=0$ matrix elements off-diagonal in F_1 were taken into consideration. The Hamiltonian matrix was then factorized into blocks of 4×4 dimension or smaller, and was numerically diagonalized in carrying out the least-squares analysis.

The observed frequencies of $^{11}B^{35}Cl$ were thus analyzed taking B_0, D_0, and $eQq(^{35}Cl)$ as adjustable parameters, while $eQq(^{11}B)$ was determined separately by simulation; the calculated spectrum was obtained by assuming a Lorentzian line shape with the line width and modulation width of 0.25 and 0.2 MHz, respectively. For $^{11}B^{37}Cl$ only B_0 and D_0 were determined since the number of the observed lines was small, while $eQq(^{37}Cl)$ was fixed to $eQq(^{35}Cl)$ multiplied by the ratio of the nuclear quadrupole moments for ^{37}Cl and ^{35}Cl (1/1.26878). The frequencies of unresolved hyperfine components were calculated by weighting each component in proportion to the square of the normalized relative intensity. The molecular constants thus determined are listed in Table 3, where B_0 and D_0 calculated from the Dunham coefficients reported by Maki *et al.*[9] are also included for comparison.

Discussion

The eQq(Cl) constants obtained for the XCl type molecules are given in Table 4, where X=B, C, N, O, and F. The same Table also includes the values for CCl, NCl, and OCl that are obtained by correcting for the effect of π-electron delocalization estimated using the observed magnetic hyperfine coupling constants. Figure 3 plots the observed and corrected eQq values, indicated by open circles and solid circles, respectively, against the electronegativity difference. As is seen, the corrected values fall on a curve which is slightly shifted from that calculated by a formula proposed by Gordy and Cook.[1] The observed eQq(Cl) value of BCl also fits well with the curve; in order to obtain a better fit, only 0.12 π-electrons are necessary

Table 4. Chlorine nuclear quadrupole coupling constants of XCl

X	n[a)]	eQq/MHz	$eQq^{corr.b)}$/MHz	
B	0	−16.74(11)	(−23)[c)]	Present
C	1	−34.26(16)	−60.10	Ref. 4
N	2	−63.13(18)	−87.16	Ref. 6
O	3	−87.95(23)	−105.73	Ref. 3
F	4	−145.871		

a) The number of electrons in the 3π orbital. b) Corrected for π-electron delocalization. See Ref 6. c) 0.12 π-electrons were assumed to be transferred from Cl to B.

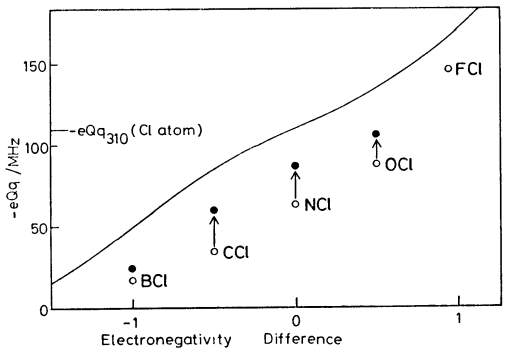

Fig. 3. The nuclear quadrupole coupling constants observed for second-row element chlorides *versus* the electronegativity difference. The observed values are shown by open circles, whereas the solid circles correspond to the corrected values. The arrows for OCl, NCl, and CCl designate the corrections for π-electron delocalization. For BCl the solid circle corresponds to 0.12 π-electron delocalization from Cl to B. The solid curve was calculated from a formula proposed by Gordy and Cook (see Ref. 1).

to be transferred from Cl to B, in other words, the 2π molecular orbital is required to involve the B $2p_\pi$ orbital by 3%. The fairly small eQq constant of BCl is thus primarily ascribed to the large ionic character of the B–Cl bond; the ionic character is estimated to be 79—85% using the relation $i_c=1+eQq/eQq_{310}$,[1] where eQq_{310} denotes the value for an atomic p electron in the 3p orbital.

The B_0 constants of both $^{11}B^{35}Cl$ and $^{11}B^{37}Cl$ which Maki *et al.*[9] have reported differ from the present, more accurate values by four times their standard errors. The discrepancy may be ascribed to the fact that almost all transitions they observed belong to the R branch and the B_0 values are likely to be subjected to systematic errors.

We have also observed a few vibrational satellites. The relative intensity of these lines indicates the effective vibrational temperature of BCl in the discharge plasma to be much higher than the room temperature, namely 1000—2000 K.

Calculations in the present study were carried out at the Computer Center of the Institute for Molecular Science.

References

1) W. Gordy and R. L. Cook, "Microwave Molecular Spectra," Interscience, New York, N. Y. (1970).
2) T. Amano, S. Saito, E. Hirota, Y. Morino, D. R. Johnson, and F. X. Powell, *J. Mol. Spectrosc.*, **30**, 275 (1969).
3) R. K. Kakar, E. A. Cohen, and M. Geller, *J. Mol. Spectrosc.*, **70**, 243 (1978).
4) Y. Endo, S. Saito, and E. Hirota, *J. Mol. Spectrosc.*, **94**, 199 (1982).
5) K. Kawaguchi, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.*, **93**, 381 (1982).
6) C. Yamada, Y. Endo, and E. Hirota, *J. Chem. Phys.*, in press.
7) B. Fabricant and J. S. Muenter, *J. Chem. Phys.*, **66**, 5274 (1977).
8) G. Herzberg and W. Hushley, *Can. J. Res., Sec. A*, **19**, 127 (1941).
9) A. G. Maki, F. J. Lovas, and R. D. Suenram, *J. Mol. Spectrosc.*, **91**, 424 (1982).
10) Y. Endo, S. Saito, and E. Hirota, *J. Chem. Phys.*, **75**, 4379 (1981).