Microwave Zeeman Spectrum of Hypochlorous Acid

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The microwave-Zeeman-spectrum of HOCl has been investigated with magnetic fields up to 25 kG. A method is described to perform the calculation of the Zeeman parameters independent from rotational constants and quadrupole coupling constants.

Introduction

In the recent years many investigations of the rotational Zeeman-effect have been reported. Among the molecules of different kinds are very few containing a chlorine atom [1–4]. We report the results of the Zeeman studies of the HOCl molecule.

Other asymmetric-top molecules containing chlorine are under investigation in this laboratory.

We started with this simple triatomic molecule, as the structure has been determined with a good approximation [5]. We hope further that quantum chemical calculations may be performed for this simple molecule.

Experimental

Hypochlorous acid (HOCl) was prepared condensing Cl_2O (0.5 ml) on ice (0.5 ml) at liquid nitrogen temperature.

The sample was then permitted to warm up to -20 to -30 °C and a slow reaction took place at the contact surface until the equilibrium mixture $Cl_2O + H_2O \rightleftarrows 2\,HOCl$ was obtained. The sample was then stored in a bath at -80 °C: a decomposition could not be detected at this temperature.

For the microwave measurements HOCl developing from the equilibrium mixture flowed continously through the waveguide at a pressure of approximately 4 mTorr and a temperature of -23 °C.

The spectrometer used was a conventional 33 kHz Stark-modulated one described elsewhere [6].

The frequency sources were conventional BWO's up to 40 GHz. For the frequency range above 50 GHz the second harmonic of a 30V12 OKI-Klystron was generated using a cross waveguide harmonic multiplier provided with a Schottky-barrier mixer diode PI 1909.

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Spectrum

HOCl is a prolate-top molecule with rotational constants $A = 607$ GHz [7], $B = 15.11750$ GHz and $C = 14.72504$ GHz [5]. Only an investigation of the μ_a-type spectrum can be performed with our present apparatus. The measured lines are: $0_{00} - 1_{01}$, $1_{11} - 2_{12}$ and $1_{10} - 2_{11}$. Due to the high values of the quadrupole coupling constants of chlorine ($\chi_{aa} = -121.91$, $\chi_{bb} = 59.61$) and the relatively low magnetic field of 30 KG only the coupled case could be investigated.

The appropriate Hamiltonian for the HOCl-molecule is in this case [8]:

$$\mathcal{H} = \mathcal{H}_{\mathrm{rot}} + \mathcal{H}_{\mathrm{mag}} + \mathcal{H}_{\mathrm{Q}}\,, \tag{1}$$

$$\mathcal{H}_{\mathrm{mag}} = \mathcal{H}^{(\mathrm{g})}_{\mathrm{mag}} + \mathcal{H}^{(\mathrm{s})}_{\mathrm{mag}} + \mathcal{H}^{(\mathrm{I})}_{\mathrm{mag}}\,. \tag{2}$$

Where $\mathcal{H}_{\mathrm{rot}}$ is the usual zero-field rigid rotor Hamiltonian, $\mathcal{H}_{\mathrm{Q}}$ is the nuclear quadrupole coupling Hamiltonian for the Cl atom and $\mathcal{H}_{\mathrm{mag}}$ describes the Zeeman effect which has three contributions: the rotational Zeeman-effect described by $\mathcal{H}^{(\mathrm{g})}_{\mathrm{mag}}$ containing the molecular g-factors, the Zeeman effect originating from the induced magnetic moment described by $\mathcal{H}^{(\mathrm{s})}_{\mathrm{mag}}$ containing the molecular magnetic susceptibility tensor and the Zeeman effect of the chlorine nucleus described by $\mathcal{H}^{(\mathrm{I})}_{\mathrm{mag}}$ containing the nuclear g-factor g_I.

Considering that the splitting due to the Zeeman effect at field strengths from 5 to 30 KG is less than or at most equal to the quadrupole coupling splitting of the chlorine atom, the cases of low and intermediate field have to be used for the calculation of the energy levels.

The combined Zeeman-quadrupole effect can be described with the basis function $|J, \tau, I, F, M_{\mathrm{F}}\rangle$ or $|J, \tau, I, M_J, M_I\rangle$.

The first one is more adapted to the case of low fields, the second one for the case of intermediate and high fields. In the $|J, \tau, I, M_I, M_J\rangle$-basis only

a $(J,\tau,I/J,\tau,I)$ submatrix will be considered. $\mathcal{H}_{\rm rot}$ is diagonal in this basis. The contributions of $\mathcal{H}_{\rm mag}$ will be considered only to first order. The $(J,\tau,I/J,\tau,I)$ submatrix has the following elements:

$$\langle J,\tau,I,M_J,M_I|\mathcal{H}_{\rm rot}+\mathcal{H}_{\rm mag}|J,\tau,I,M_J,M_I\rangle = E_{\rm rot}+E^{(g)}_{\rm mag}+E^{(S)}_{\rm mag}+E^{(I)}_{\rm mag} \tag{3}$$

where $E_{\rm rot}$ are the usual asymmetric rotor eigenvalues

$$E^{(g)}_{\rm mag} = -\mu_0\frac{M_J H_z}{J(J+1)}\sum_g g_{gg}\langle J_g^2\rangle \tag{4}$$

$$E^{(S)}_{\rm mag} = -1/2\,\chi H_z^2 - \left\{\frac{3M_J^2-J(J+1)}{3(2J-1)(2J+3)J(J+1)}\sum_g(3\chi_{gg}-3\chi)\langle J_g^2\rangle\right\} \tag{5}$$

$$E^{(I)}_{\rm mag} = -\mu_0 g_I M_I H_z \tag{6}$$

$$\langle J,\tau,I,M_J,M_I|\mathcal{H}_Q|J,\tau,I,M_J',M_I'\rangle = \frac{C}{2}\{J(J+1)-3M_J^2\}\{I(I+1)-3M_I^2\}\cdot\delta_{M_J'M_J}\,\delta_{M_I'M_I} \tag{7a}$$

$$+\tfrac{3}{4}C(2M_J\pm1)(2M_I\mp1)\sqrt{(J\mp M_J)(J\pm M_J+1)(I\pm M_I)(I\mp M_I+1)}\,\delta_{M_J',M_J\pm1}\,\delta_{M_I'M_I:\mp1} \tag{7b}$$

$$+\tfrac{3}{4}C\sqrt{(J\mp M_J)(J\mp M_J-1)(J\pm M_J+1)(J\pm M_J+2)(I\pm M_I)(I\pm M_I-1)(I\mp M_I+1)(I\mp M_I+2)}\cdot\delta_{M_J'M_J\pm2}\,\delta_{M_I'M_I\mp2} \tag{7c}$$

the value of C is:

$$C=\frac{1}{J(J+1)(2J-1)(2J+3)I(2I-1)}\sum_g\chi^{(Cl)}_{gg}\langle J_{gg}^2\rangle\,. \tag{8}$$

H_z is the applied magnetic field, μ_0 the nuclear magneton, g_{gg} the diagonal elements of the molecular g-tensor, χ_{gg} the diagonal elements of the magnetic susceptibility tensor, χ the bulk magnetic susceptibility, g_I the g-factor of the chlorine nucleus, $\chi^{(Cl)}_{gg}$ the nuclear quadrupole coupling constants of the chlorine atom and $\langle J_g^2\rangle$ the expectation value of the squared angular momentum operator for the state J,τ.

In the basis $|J,\tau,I,F,M_F\rangle$ the Hamiltonian $\mathcal{H}_Q$ of the quadrupole coupling energy is diagonal in $M_F=M_J+M_I$ and the matrix of the total Hamiltonian (1) has only diagonal elements.

In the Table 1 the submatrices for $J=0,1,2$ are given in detail with running M_J and M_I.

I is fixed to 3/2 for chlorine, $E_{\rm rot}$ and $-\frac{1}{2}\chi H_z^2$ have been omitted and M_F is given in addition to M_J and M_I indicating that the matrix is diagonal in M_F in the $|J,\tau,I,F,M_F\rangle$-basis. Due to the limitation in the strength of the applied magnetic field, it was not possible to reach the more simple case of high field condition.

For this reason the basis $|J,\tau,I,F,M_F\rangle$ has been found more convenient for the characterisation of the energy levels $E(J,\tau,I,F,M_F)$ and for comparison with the zero field values $E_{\rm rot}(J,\tau)$

$$E(J,\tau,I,F,M_F)=E_{\rm rot}(J,\tau)-\tfrac{1}{2}\chi H_z^2 - E'(J,\tau,I,F,M_F)\,. \tag{9}$$

$E'(J,\tau,I,F,M_F)$ are the eigenvalues of matrices given in Table 1.

To avoid the use of inaccurate rotational constants and of the quadrupole coupling constants of chlorine for the determination of all Zeeman parameters, a method has been developed which uses the frequency differences between measured Zeeman satellites.

Simple relations have been obtained relating the frequency differences and the g-factors only or the magnetic susceptibility anisotropies only.

		$M_F=\pm3/2$	$M_F=\pm1/2$
		$M_J=0;\ M_I=\pm3/2$	$M_J=0;M_I=\pm1/2$
$M_F=\pm3/2$	$M_J=0$ $M_I=\pm3/2$	$\mp3/2\,\mu_0 g_I H_z$	0
$M_F=\pm1/2$	$M_J=0$ $M_I=\pm1/2$	0	$\mp1/2\,\mu_0 g_I H_z$

Table 1 a. Submatrix for $J=0$.

Table 1 b. Part of the submatrix for $J=1$ with the elements used in this work.

		$M_F=\pm5/2$	$M_F=\pm3/2$	
		$M_J=\pm1;\quad M_I=\pm3/2$	$M_J=\pm1;\ M_I=\pm1/2$	$M_J=0;\ M_I=\pm3/2$
$M_F=\pm5/2$	$M_J=\pm1$ $M_I=\pm3/2$	$\mp3/2\ \mu_0\, g_I H_z$ $\mp1/2\ \mu_0 \sum_g g_{gg} \langle J_g^2\rangle_{1\tau} H_z$ $-H_z^2/30 \sum_g (3\chi_{gg}-3\chi)\ \langle J_g^2\rangle_{1\tau}$ $+1/20 \sum_g \chi_{gg}^{(Cl)} \langle J_g^2\rangle_{1\tau}$	0	0
$M_F=\pm3/2$	$M_J=\pm1$ $M_I=\pm1/2$	0	$\mp1/2\ \mu_0\, g_I H_z$ $\mp1/2\ \mu_0 \sum_g g_{gg} \langle J_g^2\rangle_{1\tau} H_z$ $-H_z^2/30 \sum_g (3\chi_{gg}-3\chi)\ \langle J_g^2\rangle_{1\tau}$ $-1/20 \sum_g \chi_{gg}^{(Cl)} \langle J_g^2\rangle_{1\tau}$	$\frac{\sqrt{6}}{20} \sum_g \chi_{gg}^{(Cl)} \langle J_g^2\rangle_{1\tau}$
	$M_J=0$ $M_I=\pm3/2$	0	$\frac{\sqrt{6}}{20} \sum_g \chi_{gg}^{(Cl)} \langle J_g^2\rangle_{1\tau}$	$\pm3/2\ \mu_0\, g_I H_z$ $+H_z^2/15 \sum_g (3\chi_{gg}-3\chi)\ \langle J_g^2\rangle_{1\tau}$ $-1/10 \sum_g \chi_{gg}^{(Cl)} \langle J_g^2\rangle_{1\tau}$

Table 1 c. Part of the submatrix for $J=2$ with the elements used in this work.

		$M_F=\pm7/2$	$M_F=\pm5/2$	
		$M_J=\pm2;\quad M_I=\pm1/3$	$M_J=\pm2;\ M_I=\pm1/2$	$M_J=\pm1;\ M_I=\pm3/2$
$M_F=\pm7/2$	$M_J=\pm2;$ $M_I=\pm3/2$	$\mp3/2\ \mu_0\, g_I H_z$ $\mp1/3\ \mu_0 \sum_g g_{gg} \langle J_g^2\rangle_{2\tau} H_z$ $-H_z^2/63 \sum_g (3\chi_{gg}-3\chi)\ \langle J_g^2\rangle_{2\tau}$ $+1/42 \sum_g \chi_{gg}^{(Cl)} \langle J_g^2\rangle_{2\tau}$	0	0
$M_F=\pm5/2$	$M_J=\pm2;$ $M_I=\pm1/2$	0	$\mp1/2\ \mu_0\, g_I H_z$ $\mp1/3\ \mu_0 H_z \sum_g g_{gg} \langle J_g^2\rangle_{2\tau}$ $-H_z^2/63 \sum_g (3\chi_{gg}-3\chi)\ \langle J_g^2\rangle_{2\tau}$ $-1/42 \sum_g \chi_{gg}^{(Cl)} \langle J_g^2\rangle_{2\tau}$	$\frac{\sqrt{3}}{42} \sum_g \chi_{gg}^{(Cl)} \langle J_g^2\rangle_{2\tau}$
	$M_J=\pm1;$ $M_I=\pm3/2$	0	$\frac{\sqrt{3}}{42} \sum_g \chi_{gg}^{(Cl)} \langle J_g^2\rangle_{2\tau}$	$\mp3/2\ \mu_0\, g_I H_z$ $\mp1/6\ \mu_0 H_z \sum_g g_{gg} \langle J_g^2\rangle_{2\tau}$ $+H_z^2/126 \sum_g (3\chi_{gg}-3\chi)\ \langle J_g^2\rangle_{2\tau}$ $-1/84 \sum_g \chi_{gg}^{(Cl)} \langle J_g^2\rangle_{2\tau}$

Thus the values of these parameters are determined from experimental results directly without using involved fitting procedures.

The following procedure is used in the case of parallel fields with $\Delta M_F = 0$: The transition frequency from the level $E(J, \tau, I, F, M_F)$ to the level $E'(J', \tau', I', F, M_F')$ is expressed by the notation $\nu(J_\tau \rightarrow J'_{\tau'}; F \rightarrow F'; M_F; H_z)$. Further we use the sum of the transition frequencies

$$\nu[J_\tau \rightarrow (J+1)_{\tau'}; F = J+I \rightarrow F' = F+1; M_F = F; H_z]$$

and

$$\nu[J_\tau \rightarrow (J+1)_{\tau'}; F = J+I \rightarrow F' = F; M_F = F; H_z]$$

in the following formula

$$\nu^{\pm}(M_F = \pm F) = \frac{\nu(J_\tau \rightarrow J'_{\tau'};\ F = J+I \rightarrow F' = F+1; M_F = \pm F; H_z) + \nu(J_\tau \rightarrow J'_{\tau'};\ F = J+I \rightarrow F' = F; M_F = \pm F; H_z)}{2}. \tag{10}$$

Now it is easy to see that

$$\nu^-(M_F = -F) - \nu^+(M_F = +F) = D_\nu^- = \mu_0 \frac{H_z}{h} \Delta \quad \text{where} \quad \Delta = f(g_I, g_{aa}, g_{bb}, g_{cc}) \tag{11}$$

is only a function of g_I and g-factors.

For the susceptibility anisotropies the following formula was developed:

$$[\nu^-(M_F = -F) + \nu^+(M_F = +F)]_{H_z \neq 0} - [\nu^-(M_F = -F) + \nu^+(M_F = +F)]_{H_z = 0} = D_\nu^+ = \frac{H_z^2}{h} S \tag{12}$$

where $S = f(\alpha, \beta)$, $\alpha = 2\chi_{aa} - \chi_{bb} - \chi_{cc}$ and $\beta = 2\chi_{bb} - \chi_{cc} - \chi_{aa}$.

Both Δ and S functions are given in Table 2.

In the case of perpendicular field conditions ($\Delta M_F = \pm 1$) the following formulas have been found

$$\begin{aligned} &\nu[J_\tau \rightarrow (J+1)_{\tau'};\ F = J+I \rightarrow F' = F+1;\ M_F = -F \rightarrow M_F' = -(F+1);\ H_z] \\ &\quad - \nu[J_\tau \rightarrow (J+1)_{\tau'};\ F = J+I \rightarrow F' = F+1;\ M_F = F \rightarrow M_F' = F+1;\ H_z] \\ &= [\nu(\Delta M_F = -1) - \nu(\Delta M_F = +1)] = D_\nu^- = \mu_0 \frac{H_z}{h} \Delta \end{aligned} \tag{13}$$

$$[\nu(\Delta M_F = -1) + \nu(\Delta M_F = +1)]_{H_z \neq 0} - [\nu(\Delta M_F = -1) + \nu(\Delta M_F = +1)]_{H_z = 0} = D_\nu^+ = \frac{H_z^2}{h} S. \tag{14}$$

Further, for the $0_{00} - 1_{01}$ transition the formulas given in the appendix were developed.

Using the relations (11, 12), (13, 14) and (A1, A2) the values of the g-factors and of the magnetic susceptibility anisotropies could be obtained. The Zeeman splittings at several magnetic fields of those transitions used to derive the functions (see Table 2) are given in Table 3 together with the D_ν^+ and D_ν^- values.

The assignment was made observing the relative intensities and the frequency shifts of each Zeeman component. $D_\nu^\pm$ values smaller than 30 kHz have been omitted, as the experimental errors of $D_\nu^\pm$ have been estimated to be about ± 20 kHz. From

Table 2. List of the obtained functions $\Delta_i(g_I, g_{aa}, g_{bb}, g_{cc})$ and $S_i(\alpha, \beta)$. Nr. 1 and 2 refer to $\Delta M_F = 0$ case Nr. 3, 4, 5 and 6 to the $\Delta M_F = \pm 1$ case.

i	Transition	F	$\lvert M_F \rvert \rightarrow \lvert M_F' \rvert$	$\Delta(g_I, g_{aa}\, g_{bb}\, g_{cc})$	$S(\alpha, \beta)$
1	$0_{00} \rightarrow 1_{01}$	3/2	3/2 → 3/2	$-g_I + 1/2(g_{bb} + g_{cc})$	$-\alpha/30$
2	$1_{11} \rightarrow 2_{12}$	5/2	5/2 → 5/2	$-g_I - 1/2\, g_{aa} + 1/2\, g_{bb} + g_{cc}$	$(5\alpha - 9\beta)/210$
3	$0_{00} \rightarrow 1_{01}$	3/2	3/2 → 5/2	$g_{bb} + g_{cc}$	$\alpha/15$
4	$1_{11} \rightarrow 2_{12}$	5/2	5/2 → 7/2	$1/3(-g_{aa} + 2\, g_{bb} + 5\, g_{cc})$	$(10\alpha + 3\beta)/105$
5	$1_{10} \rightarrow 2_{11}$	5/2	5/2 → 7/2	$1/3(-g_{aa} + 5\, g_{bb} + 2\, g_{cc})$	$(7\alpha - 3\beta)/105$
6	$0_{00} \rightarrow 1_{01}$	3/2	1/2 → 3/2	$g_I + 1/2(g_{bb} + g_{cc})$	$-\alpha/30$

Table 3. Observed D_ν^- and D_ν^+ values.

$J \to J'$	Field (Gauss)	$F \to F'$	$M_F \to M_{F'}$	Obs. Freq. (MHz)	$F \to F'$	$M_F \to M_{F'}$	Obs. Freq. (MHz)	D_ν^- (MHz) obs.	D_ν^- (MHz) calc. *	D_ν^+ (kHz) obs.	D_ν^+ (kHz) calc. *
$0_{00} \to 1_{01}$	0.0	3/2 → 5/2		29848.586	3/2 → 3/2		29818.063				
	13023.1	3/2 → 5/2	3/2 → 3/2 −3/2 → −3/2	29852.531 29845.232	3/2 → 3/2	3/2 → 3/2 −3/2 → −3/2	29820.279 29815.328	−6.125	−6.129	—	—
	19117.1	3/2 → 5/2	3/2 → 3/2 −3/2 → −3/2	29854.550 29843.893	3/2 → 3/2	3/2 → 3/2 −3/2 → −3/2	29821.168 29813.830	−8.998	−8.998	72	78
	24078.9	3/2 → 5/2	3/2 → 3/2 3/2 → 3/2	29856.263 29842.937	3/2 → 3/2	3/2 → 3/2 −3/2 → −3/2	29821.851 29812.504	−11.337	−11.334	129	124
	9820.9	3/2 → 5/2	3/2 → 5/2 −3/2 → −5/2	29849.075 29848.043				−1.032	−1.031	—	—
	14707.3	3/2 → 5/2	3/2 → 5/2 −3/2 → −5/2	29849.305 29847.765				−1.540	−1.543	−102	−104
	21966.5	3/2 → 5/2	3/2 → 5/2 −3/2 → −5/2	29849.623 29847.317				−2.305	−2.305	−232	−232
	14707.3	3/2 → 5/2	1/2 → 3/2 −1/2 → −3/2	29846.942 29850.995	3/2 → 3/2	1/2 → 3/2 −1/2 → −3/2	29814.395 29821.070	5.364	5.364	—	—
$1_{11} \to 2_{12}$	0.0	5/2 → 7/2		59295.709	5/2 → 5/2		59280.108				
	6511.7	5/2 → 7/2	5/2 → 5/2 −5/2 → −5/2	59298.053 59293.605	5/2 → 5/2	5/2 → 5/2 −5/2 → −5/2	59282.592 59277.425	−4.808	−4.812	—	—
	13002.0	5/2 → 7/2	5/2 → 5/2 −5/2 → −5/2	59300.525 59291.630	5/2 → 5/2	5/2 → 5/2 −5/2 → −5/2	59284.868 59274.540	−9.612	−9.609	—	—
	9824.3	5/2 → 7/2	5/2 → 7/2 −5/2 → −7/2	59297.075 59294.324				−2.751	−2.739	—	—
	14702.9	5/2 → 7/2	5/2 → 7/2 −5/2 → −7/2	59297.710 59293.629				−4.081	−4.098	−79	−95
	21966.1	5/2 → 7/2	5/2 → 7/2 −5/2 → −7/2	59298.658 59292.531				−6.127	−6.121	−229	−222
$1_{10} \to 2_{11}$	0.0	5/2 → 7/2		60077.657							
	9833.2	5/2 → 7/2	5/2 → 7/2 −5/2 → −7/2	60079.065 60076.211				−2.854	−2.850	—	—
	14704.2	5/2 → 7/2	5/2 → 7/2 −5/2 → −7/2	60079.737 60075.465				−4.272	−4.258	−112	−113
	21968.7		5/2 → 7/2 −5/2 → −7/2	60080.703 60074.357				−6.346	−6.358	−254	−253

* These values have been calculated by putting the values listed in Table 3 into the relation,

$$D_\nu^- = 0.76227_2 \times 10^{-3} \times \Delta \times H_z \text{ and } D_\nu^+ = \frac{1}{3.99027} \times S \times H_z^2 .$$

D_v^+ and D_v^--values the functions Δ and S could be estimated using a least square fitting procedure. They are listed in Table 4.

Table 4. The value of the functions shown in Table 2.

Functions		obs.	dev. *
Δ_1	=	-0.6176 ± 0.0024	-0.0002
Δ_2	=	-0.9697 ± 0.0007	-0.0002
Δ_3	=	-0.1376 ± 0.0002	-0.0022
$3\,\Delta_4$	=	-1.0964 ± 0.0038	0.0007
$3\,\Delta_5$	=	-1.1377 ± 0.0035	0.0003
Δ_6	=	0.4786 ± 0.0010	0.0009
$S\cdot 30$	=	26.2 ± 2.2 **	1.4
$S\cdot 15$	=	-28.9 ± 0.3	-4.1
$S\cdot 105$	=	-220.7 ± 2.2	0.4
$S\cdot 105$	=	-200.5 ± 24.1	0.3

* dev. are the differences between the observed and the calculated values.
** The units are 10^{-6} erg/G²·mole.

The signs of the g-factors, as listed in Table 6 could be determined using the knowledge that the sign of the g_I-value of chlorine is positive [10].

In this case no reference to the magnitude of the molecular electric quadrupole moment or the sign of the second moment of the electric charge is necessary.

The electric quadrupole coupling constants of the chlorine atom were remeasured from the frequency splitting of the $0_{00}-1_{01}$, $1_{11}-2_{12}$ and $1_{10}-2_{11}$ transitions at zero magnetic field as reported in Table 5. The results, listed in Table 6, agree with the values reported by Mirri et al. [5] within experimental errors. For a final check the frequency splittings observed for the $0_{00}-1_{01}$, $1_{11}-2_{12}$, $1_{10}-2_{11}$ and $1_{01}-2_{02}$ transitions are listed again in Table 7 for both $\Delta M_F = 0$ and $\Delta M_F = \pm 1$ cases and compared with calculated values which were obtained by solving the Hamiltonian (2). In these calculations the values reported by Ashby [8] were taken for the rotational constant A and those reported by Mirri et al. [5] for the constants B and C.

Table 6. Chlorine nuclear g_I-factor, molecular g-values, magnetic susceptibility anisotropy parameters and nuclear quadrupole constants of chlorine.

g_I	=	0.5490 ± 0.0014
g_{aa}	=	0.6390 ± 0.0055
g_{bb}	=	-0.0752 ± 0.0009
g_{cc}	=	-0.0616 ± 0.0010
$2\,\chi_{aa}-\chi_{bb}-\chi_{cc}$	=	$-24.8 \pm 0.3 \cdot 10^{-6}$ erg/G²·mole
$2\,\chi_{bb}-\chi_{cc}-\chi_{aa}$	=	$15.8 \pm 0.7 \cdot 10^{-6}$ erg/G²·mole
$\chi_{aa}^{(Cl)}$	=	-121.93 ± 0.03 MHz $(-121.91 \pm 0.07$ MHz),
$\chi_{bb}^{(Cl)}$	=	59.50 ± 0.04 MHz $(59.61 \pm 0.08$ MHz)
$\chi_{cc}^{(Cl)}$	=	62.43 MHz

The values in parenthesis are given in a preceeding work from Mirri et al. Our values fit the measurements of this paper in a better way.

Molecular Electric Quadrupole Moment

Combining the molecular g-values, the magnetic susceptibility anisotropies and the rotational constants, the diagonal elements of the molecular electric quadrupole moment tensor can be calculated using Eq. (15)

$$Q_{aa} = -\frac{\hbar\,|e|}{8\pi M_p}\left(\frac{2\,g_{aa}}{A}-\frac{g_{bb}}{B}-\frac{g_{cc}}{C}\right)-\frac{2\,m\,c^2}{|e|}\,(2\,\chi_{aa}-\chi_{bb}-\chi_{cc}) \qquad (15)$$

Table 5. Transition frequencies (MHz) at zero magnetic fields.

$J_{K-K+}\rightarrow J'_{K-K+}$	corr. *	$F\rightarrow F'$	obs.	calc.
$0_{00}\rightarrow 1_{01}$	29842.461 ±0.011	3/2 → 1/2	29872.925	29872.943
		3/2 → 5/2	29848.586	29848.557
		3/2 → 3/2	29818.063	29818.075
$1_{11}\rightarrow 2_{12}$	59288.274 ±0.008	1/2 → 1/2	59318.759	59318.756
		1/2 → 3/2	59303.141	59303.149
		5/2 → 7/2	59295.709	59295.708
		5/2 → 5/2	59280.108	59280.101
		3/2 → 3/2	59276.366	59276.373
		3/2 → 5/2	59265.229	59265.226
$1_{10}\rightarrow 2_{11}$	60070.256 ±0.008	1/2 → 1/2	60100.719	60100.738
		1/2 → 3/2	60085.880	60085.863
		5/2 → 7/2	60077.657	60077.628
		5/2 → 5/2	60062.733	60062.752
		3/2 → 3/2	60057.764	60057.771
		3/2 → 5/2	60047.144	60047.145
$1_{01}\rightarrow 2_{02}$	59684.064 ±0.013	3/2 → 3/2	59708.463	59708.450
		5/2 → 5/2	59656.181	59656.195

* corr. are the corrected frequencies for the nuclear quadrupole splittings.

Table 7. Zeeman splittings $\Delta\nu_0$ with respect to the unperturbed line at parallel and perpendicular fields.

$J_{K-K+} \rightarrow J'_{K-K+}$	$F \rightarrow F'$	$M_F \rightarrow M_{F'}$	Field (Gauss)	$\Delta\nu_0$ (MHz) obs.	$\Delta\nu_0$ (MHz) calc.
(parallel field)					
$0_{00} \rightarrow 1_{01}$	$3/2 \rightarrow 1/2$	$-1/2 \rightarrow -1/2$	24078.1	4.936	4.943
		$1/2 \rightarrow 1/2$	24078.1	−2.314	−2.316
	$3/2 \rightarrow 5/2$	$3/2 \rightarrow 3/2$	24078.9	7.676	7.684
		$1/2 \rightarrow 1/2$	24078.9	3.608	3.616
		$-1/2 \rightarrow -1/2$	24078.9	−0.753	−0.754
		$-3/2 \rightarrow -3/2$	24078.9	−5.649	−5.654
	$3/2 \rightarrow 3/2$	$3/2 \rightarrow 3/2$	24078.9	3.788	3.767
		$-3/2 \rightarrow -3/2$	24078.9	−5.559	−5.558
$1_{11} \rightarrow 2_{12}$	$1/2 \rightarrow 1/2$	$1/2 \rightarrow 1/2$	13002.0	7.136	7.162
		$-1/2 \rightarrow -1/2$	13002.0	−3.839	−3.844
	$1/2 \rightarrow 3/2$	$1/2 \rightarrow 1/2$	13002.0	3.052	3.035
		$-1/2 \rightarrow -1/2$	13002.0	−2.912	−2.951
	$5/2 \rightarrow 7/2$	$5/2 \rightarrow 5/2$	13002.0	4.816	4.802
		$3/2 \rightarrow 3/2$	13002.0	3.602	3.593
		$-3/2 \rightarrow -3/2$	13002.0	−1.847	−1.882
		$-5/2 \rightarrow -5/2$	13002.0	−4.079	−4.110
	$5/2 \rightarrow 5/2$	$5/2 \rightarrow 5/2$	13002.0	4.760	4.735
		$-5/2 \rightarrow -5/2$	13002.0	−5.568	−5.534
	$3/2 \rightarrow 3/2$	$3/2 \rightarrow 3/2$	13002.0	5.474	5.519
		$-1/2 \rightarrow -1/2$	13002.0	−2.206	−2.209
		$-3/2 \rightarrow -3/2$	13002.0	−3.914	−3.888
	$3/2 \rightarrow 5/2$	$3/2 \rightarrow 3/2$	12999.9	1.956	1.959
		$1/2 \rightarrow 1/2$	12999.9	−1.314	−1.326
		$-1/2 \rightarrow -1/2$	12999.9	−3.828	−3.850
		$-3/2 \rightarrow -3/2$	12999.9	−5.414	−5.417
$1_{10} \rightarrow 2_{11}$					
	$1/2 \rightarrow 1/2$	$-1/2 \rightarrow -1/2$	24080.6	−3.584	−3.603
	$1/2 \rightarrow 3/2$	$1/2 \rightarrow 1/2$	24080.6	5.131	5.148
	$5/2 \rightarrow 7/2$	$1/2 \rightarrow 1/2$	19107.0	3.854	3.873
		$-1/2 \rightarrow -1/2$	19107.0	0.849	0.854
		$-3/2 \rightarrow -3/2$	19107.0	−2.077	−2.061
		$-5/2 \rightarrow -5/2$	19107.0	−5.829	−5.804
	$5/2 \rightarrow 5/2$	$5/2 \rightarrow 5/2$	19117.1	6.683	6.702
		$3/2 \rightarrow 3/2$	19117.1	1.718	1.709

$J_{K-K+} \rightarrow J'_{K-K+}$	$F \rightarrow F'$	$M_F \rightarrow M_{F'}$	Field (Gauss)	$\Delta\nu_0$ (MHz) obs.	$\Delta\nu_0$ (MHz) calc.
(parallel field)					
	$3/2 \rightarrow 3/2$	$3/2 \rightarrow 3/2$	19107.0	7.854	7.838
		$-1/2 \rightarrow -1/2$	19107.0	−4.212	−4.225
		$-3/2 \rightarrow -3/2$	19107.0	−5.406	−5.418
	$3/2 \rightarrow 5/2$	$3/2 \rightarrow 3/2$	19107.0	1.986	2.001
		$1/2 \rightarrow 1/2$	19107.0	−3.365	−3.354
$1_{01} \rightarrow 2_{02}$		$-1/2 \rightarrow -1/2$	19107.0	−7.308	−7.325
	$3/2 \rightarrow 3/2$	$3/2 \rightarrow 3/2$	24074.4	11.501	11.512
		$-1/2 \rightarrow -1/2$	24074.4	−1.314	−1.321
		$-3/2 \rightarrow -3/2$	24074.4	−5.274	−5.276
(perpendicular field)					
$0_{00} \rightarrow 1_{01}$	$3/2 \rightarrow 1/2$	$3/2 \rightarrow 1/2$	14707.3	4.356	4.367
		$-3/2 \rightarrow -1/2$	14707.3	−3.382	−3.399
		$-1/2 \rightarrow 1/2$	14707.3	−7.921	−7.942
	$3/2 \rightarrow 5/2$	$-1/2 \rightarrow -3/2$	14707.3	2.409	2.416
		$3/2 \rightarrow 5/2$	14707.3	0.719	0.722
		$-3/2 \rightarrow -5/2$	14707.3	−0.821	−0.811
		$1/2 \rightarrow 3/2$	14707.3	−1.645	−1.650
		$-1/2 \rightarrow 1/2$	14707.3	−4.205	−4.213
	$3/2 \rightarrow 3/2$	$3/2 \rightarrow 1/2$	14707.3	5.994	6.001
		$\mathbf{1/2 \rightarrow -1/2}$	14707.3	4.172	4.187
		$-1/2 \rightarrow -3/2$	14707.3	3.007	3.017
		$1/2 \rightarrow 3/2$	14707.3	−3.668	−3.694
		$-1/2 \rightarrow 1/2$	14707.3	−6.290	−6.309
$1_{11} \rightarrow 2_{12}$					
	$1/2 \rightarrow 1/2$	$-1/2 \rightarrow 1/2$	14702.9	0.173	0.183
	$5/2 \rightarrow 7/2$	$5/2 \rightarrow 7/2$	14702.9	2.001	1.997
		$3/2 \rightarrow 5/2$	14700.8	0.625	0.679
		$-3/2 \rightarrow -5/2$	14700.8		0.541
		$1/2 \rightarrow 3/2$	14700.8	−0.625	−0.649
		$-5/2 \rightarrow -7/2$	14702.9	−2.080	−2.101
	$3/2 \rightarrow 5/2$	$3/2 \rightarrow 5/2$	14700.2	0.773	0.793
		$1/2 \rightarrow -1/2$	14700.2		0.711
		$-1/2 \rightarrow -3/2$	14700.2	−1.238	−1.268
		$-3/2 \rightarrow -5/2$	14700.2	−1.968	−1.980
$1_{10} \rightarrow 2_{11}$	$1/2 \rightarrow 1/2$	$-1/2 \rightarrow 1/2$	14704.7	0.366	0.324
	$5/2 \rightarrow 7/2$	$5/2 \rightarrow 7/2$	14704.7	2.080	2.069
		$3/2 \rightarrow 5/2$	14704.7	0.778	0.768
		$-3/2 \rightarrow -5/2$	14704.7	0.553	0.583
		$1/2 \rightarrow 3/2$	14704.7	−0.467	−0.489
		$-5/2 \rightarrow -7/2$	14704.7	−2.192	−2.185
	$3/2 \rightarrow 5/2$	$3/2 \rightarrow 5/2$	14704.7	0.855	0.837
		$-1/2 \rightarrow -3/2$	14704.7	−1.491	−1.471
		$-3/2 \rightarrow -5/2$	14704.7	−2.088	−2.127

and cyclic, where $|e|$ is the electronic charge, M_p the proton mass, m the electron mass. A, B and C are rotational constants, g_{gg} the molecular g-factors and χ_{gg} the magnetic susceptibilities. The Q_{gg} are given in Table 8.

The second moment of the electron charge can be calculated in the form given as follows:

$$\langle b^2\rangle - \langle a^2\rangle = \sum_n Z_n(b_n^2 - a_n^2) + \frac{\hbar}{4\pi M_p}\left(\frac{g_{bb}}{B} - \frac{g_{aa}}{A}\right) + \frac{4mc^2}{3e^2}\left[(2\chi_{bb} - \chi_{aa} - \chi_{cc}) - (2\chi_{aa} - \chi_{bb} - \chi_{cc})\right] \tag{16}$$

$$\langle a^2\rangle = \langle 0 \,|\, \Sigma a_i^2 \,|\, 0\rangle \tag{17}$$

Table 8. Diagonal elements of the molecular electric quadrupole moment tensor.

Q_{aa}	$= +(0.50 \pm 0.35)\cdot 10^{-26}$ esu
Q_{bb}	$= +(0.74 \pm 0.67)\cdot 10^{-26}$ esu
Q_{cc}	$= -(1.24 \pm 1.02)\cdot 10^{-26}$ esu

where Z_n is the atomic number of the nth nucleus, a_n and b_n are its coordinates in the principal axes, a_i is the coordinate of the i^{th} electron.

$\langle c^2\rangle - \langle b^2\rangle$ and $\langle a^2\rangle - \langle c^2\rangle$ are obtained by cyclic permutations.

Using nuclear second moments calculated from the known structure of HOCl [5]:

$$\sum_n Z_n a_n^2 = (17.41 \pm 0.04)\cdot 10^{-16}\,\text{cm}^2,$$
$$\sum_n Z_n b_n^2 = (0.81 \pm 0.03)\cdot 10^{-16}\,\text{cm}^2,$$
$$\sum_n Z_n c_n^2 = 0.0$$

and the empirical rule given in (9) for the estimation of $\langle c^2\rangle$ from free atom values, one gets the values given in Table 9. Further the diagonal elements of the paramagnetic susceptibility tensor and of the diamagnetic susceptibility tensor given by the following formulas, could be calculated.

$$\chi_{aa}^p = -\left(\frac{e^2 N}{2mc^2}\right)\left[\left(\frac{\hbar\, g_{aa}}{8\pi A M_p}\right) - \tfrac{1}{2}\sum_n Z_n(b_n^2 + c_n^2)\right] \tag{18}$$

$$\chi_{aa}^d = -\left(\frac{e^2 N}{4mc^2}\right)\langle 0 \,|\, \sum (b^2 + c^2) \,|\, 0\rangle\,. \tag{19}$$

Table 9 lists all the calculated parameters. As the bulk magnetic susceptibility is the sum of a paramagnetic and a diamagnetic term it can be now evaluated to be

$$\chi = -(27.2 \pm 3.7)\cdot 10^{-6}\,\text{erg/G}^2\cdot\text{mole}\,.$$

Table 9. Calculated Zeeman-parameters.

$\langle a^2\rangle$	21.3 ±0.5
$\langle b^2\rangle$	4.8 ±0.5
$\langle c^2\rangle$	3.9 (±0.3) *
$\langle \chi_{aa}^d\rangle$	−(36.7 ±3.2)
$\langle \chi_{bb}^d\rangle$	−(106.3 ±3.2)
$\langle \chi_{cc}^p\rangle$	−(110.4 ±3.9)
$\langle \chi_{aa}^p\rangle$	1.2 ±0.2
$\langle \chi_{bb}^d\rangle$	84.4 ±0.3
$\langle \chi_{cc}^p\rangle$	86.2 ±0.4
χ_{aa}	−(35.5 ±3.4)
χ_{bb}	−(21.9 ±3.5)
χ_{cc}	−(24.2 ±4.3)
$\chi = 1/3(\chi_{aa} + \chi_{bb} + \chi_{cc})$	−(27.2 ±3.7)

* Estimated with the additivity rule given in Reference 9. χ-values are given in units of 10^{-6} erg/G²·mole. $\langle a^2\rangle$, $\langle b^2\rangle$ and $\langle c^2\rangle$ are given in units of 10^{-16} cm².

Appendix

For the transition $0_{00} \rightarrow 1_{01}$ ($i = 6$ in Table 2) the following formulas were developed:

$$\nu(F = 3/2 \rightarrow F' = 5/2;\ M_F = -1/2 \rightarrow M_F' = -3/2;\ H_z) = \nu_1\,,$$
$$\nu(F = 3/2 \rightarrow F' = 3/2;\ M_F = -1/2 \rightarrow M_F' = -3/2;\ H_z) = \nu_2\,,$$
$$\nu(F = 3/2 \rightarrow F' = 5/2;\ M_F = 1/2 \rightarrow M_F' = 3/2;\ H_z) = \nu_3\,,$$
$$\nu(F = 3/2 \rightarrow F' = 3/2;\ M_F = 1/2 \rightarrow M_F' = 3/2;\ H_z) = \nu_4;$$

$$D_\nu^- = \frac{\nu_1 + \nu_2}{2} - \frac{\nu_3 + \nu_4}{2} = \mu_0(H_z/h)\,\Delta, \tag{A1}$$

$$D_\nu^+ = \left[\frac{\nu_1+\nu_2}{2}+\frac{\nu_3+\nu_4}{2}\right]_{H_z\neq 0} - \left[\frac{\nu_1+\nu_2}{2}+\frac{\nu_3+\nu_4}{2}\right]_{H_z=0} = \frac{H_z^2}{h} S\,. \qquad \text{(A 2)}$$

Δ and S are listed in Table 2.

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