

Microwave Spectrum of Chlorine Dioxide. II. Analysis of Hyperfine Structure and the Spectrum of $\text{Cl}^{35}\text{O}^{16}\text{O}^{18}\dagger$

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 (Received July 24, 1961)

The hyperfine structure of the microwave spectra of Cl^{35}O_2 and Cl^{37}O_2 has been analyzed. It was found possible to fit the hyperfine splitting within experimental error with the Hamiltonian:

$$H = AN_a^2 + BN_b^2 + CN_c^2 + (0)_S(\mathbf{N} \cdot \mathbf{S}) + \sum_{i,j} (ij)_S N_i S_j + (0)_I(\mathbf{S} \cdot \mathbf{I}) + \sum_{i,j} (ij)_I S_i I_j + \sum_{i,j} (ij)_Q I_i I_j.$$

Also, several rotational transitions of $\text{Cl}^{35}\text{O}^{16}\text{O}^{18}$ have been observed and assigned.

A ROTATIONAL assignment of the microwave spectrum chlorine dioxide has been previously reported.¹ The present work is largely concerned with fitting the hyperfine structure, which was only approximately treated in I, as exactly as possible. The results of the present investigation completely confirm both the rotational assignment and the hyperfine assignment given in I. In addition the approximate interaction constants given in I are fairly close to the final constants given here.

THE HYPERFINE HAMILTONIAN

For an asymmetric rotor molecule with $S = \frac{1}{2}$ and one nuclear spin, the Hamiltonian for the rotational and electronic spin and nuclear spin states can be expressed as follows²⁻⁴:

$$H = AN_a^2 + BN_b^2 + CN_c^2 + (0)_S(\mathbf{N} \cdot \mathbf{S}) + \sum_{i,j} (ij)_S N_i S_j + \sum_{i,j,k} (k)_S [e_{ijk} N_i S_j + i\hbar S_k] + (0)_I(\mathbf{S} \cdot \mathbf{I}) + \sum_{i,j,k} (ij)_I S_i I_j + \sum_{i,j,k} e_{ijk} (i)_I S_j I_k + \sum_{i,j} (ij)_Q I_i I_j. \quad (1)$$

The quantity \mathbf{N} (with components N_a, N_b, N_c) is the rotational angular momentum operator. Similarly, \mathbf{S} is the electronic spin operator. The quantities $(ij)_S, (ij)_I, (ij)_Q$ are components of symmetric, traceless, second-rank tensors which are constants in the frame rotating with the molecule. The quantities $(k)_S$ and $(i)_I$ are components of an axial vector which is a constant in the molecular frame.

[†] This work was supported by a grant to Rice University from the Robert A. Welch Foundation.

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¹ R. F. Curl, J. L. Kinsey, J. G. Baker, J. C. Baird, G. R. Bird, R. F. Heidelberg, T. M. Sudgen, D. R. Jenkins, and C. N. Kenney, *Phys. Rev.* **121**, 1119 (1961). Henceforth this will be referred to as I.

² R. F. Curl and J. L. Kinsey, *J. Chem. Phys.* **35**, 1758 (1961).

³ C. C. Lin, *Phys. Rev.* **116**, 903 (1959).

⁴ J. G. Baker, thesis, Cambridge, 1958 (unpublished).

For the case of $\text{Cl}^{35}\text{O}_2^{16}$ and $\text{Cl}^{37}\text{O}_2^{16}$ with C_{2v} symmetry, by symmetry one has $(i)_S = (i)_I = 0$, $i = a, b, c$ and the tensors $(ij)_S, (ij)_I, (ij)_Q$ are diagonal. In the case of $\text{Cl}^{35}\text{O}^{16}\text{O}^{18}$, the symmetry is broken slightly. However, the terms which now appear contribute nothing in first-order perturbation and are neglected. The final justification of this approximation is the experimental fact that the hyperfine structure of $\text{Cl}^{35}\text{O}^{16}\text{O}^{18}$ is virtually identical with that of $\text{Cl}^{35}\text{O}_2^{16}$. Therefore the final Hamiltonian form used for ClO_2 is

$$H = AN_a^2 + BN_b^2 + CN_c^2 + (0)_S(\mathbf{N} \cdot \mathbf{S}) + (aa)_S N_a S_a + (bb)_S N_b S_b + (cc)_S N_c S_c + (0)_I(\mathbf{S} \cdot \mathbf{I}) + (aa)_I S_a I_a + (bb)_I S_b I_b + (cc)_I S_c I_c + (aa)_Q I_a^2 + (bb)_Q I_b^2 + (cc)_Q I_c^2, \quad (2)$$

where

$$(aa)_S + (bb)_S + (cc)_S = 0, \\ (aa)_I + (bb)_I + (cc)_I = 0, \\ (aa)_Q + (bb)_Q + (cc)_Q = 0.$$

The S subscript terms arise from a Van Vleck perturbation with excited electronic levels. The Fermi or contact interaction is

$$(0)_I = (16\pi/3) g_I \mu_B \mu_N |\psi(0)|^2,$$

the magnetic dipole-dipole term is

$$(ii)_I = -g_S g_I \mu_B \mu_N \langle (1 - 3r_i^2)/r^3 \rangle_{av},$$

and the quadrupole term is

$$(ii)_Q = \frac{eQ}{2I(2I-1)} \frac{\partial^2 V}{\partial x_i^2}. \quad (3)$$

CHOICE OF BASIS AND PERTURBATION TREATMENT

The rotational angular momentum \mathbf{N} , the electronic spin \mathbf{S} , and the nuclear spin \mathbf{I} , may couple in three different ways.

$$\begin{aligned} J \text{ scheme: } & \mathbf{N} + \mathbf{S} = \mathbf{J}, & \mathbf{J} + \mathbf{I} = \mathbf{F}; \\ E \text{ scheme: } & \mathbf{N} + \mathbf{I} = \mathbf{E}, & \mathbf{E} + \mathbf{S} = \mathbf{F}; \\ G \text{ scheme: } & \mathbf{I} + \mathbf{S} = \mathbf{G}, & \mathbf{G} + \mathbf{N} = \mathbf{F}. \end{aligned}$$

TABLE I. Fit of nuclear hyperfine structure.

	Cl ³⁵ O ₂		Cl ³⁷ O ₂		Cl ³⁵ O ₂ second order corrections ^b			
	$\nu(\text{obs})^a$ (Mc/sec)	ν_{\pm} (Mc/sec)	$\nu(\text{obs})^a$ (Mc/sec)	ν_{\pm} (Mc/sec)	ϵ'	ϵ (Mc/sec)	ϵ'	ϵ'
1 ₀₁ → 1 ₁₀								
J = $\frac{3}{2}$ → $\frac{3}{2}$								
F = 1 → 0	43 416.10 (+0.50)		42 112.40 (+0.23)		0	-3.2	0	0
0 → 1								
1 → 1	43 428.72 (-0.11)	43 389.28			-2.6	-3.2	0	0
2 → 1	43 398.08 (+0.08)		42 096.40 (+0.17)	42 089.51	-2.6	-3.6	0	0
1 → 2	43 444.10 (-0.14)		42 135.12 (+0.05)		-6.5	-3.2	0	0
2 → 2	43 413.60 (-0.05)		42 109.20 (-0.07)		-6.5	-3.6	0	0
3 → 2	43 338.16 (-0.42)		42 047.54 (-0.40)		-6.5	0	0	0
2 → 3	43 423.60 (+0.55)		42 117.52 (+0.37)		0	-3.6	0	0
3 → 3	43 348.60 (-0.21)		42 055.84 (-0.06)		0	0	0	0
J = $\frac{3}{2}$ → $\frac{1}{2}$								
F = 0 → 1								
1 → 1	44 545.80 (-0.12)		43 227.26 (-0.12)		2.6	-3.2	0	0
2 → 1	44 515.28 (-0.04)		43 201.54 (-0.25)		2.6	-3.6	0	0
1 → 2								
2 → 2	44 703.00 (-0.03)				6.5	-3.6	0	0
3 → 2	44 627.20 (+0.00)		43 294.8 (-0.11)		6.5	0	0	0
		ΔE ₁₀₁ = -159.0		ΔE ₁₀₁ = -158.9				
J = $\frac{1}{2}$ → $\frac{3}{2}$								
F = 1 → 0	43 112.78 (+0.17)				0	3.2	0	0
1 → 1	43 124.95 (-0.03)				-2.6	3.2	0	0
2 → 1								
1 → 2	43 140.30 (+0.04)		41 856.53 (-0.17)		-6.5	3.2	0	0
2 → 2	43 274.56 (-0.03)		41 968.48 (+0.01)		-6.5	3.6	0	0
2 → 3	43 285.5 (-0.33)		41 977.60 (-0.55)		0	3.6	0	0
J = $\frac{1}{2}$ → $\frac{1}{2}$								
F = 1 → 1	44 242.08 (-0.05)		42 948.50 (+0.09)		2.6	3.2	0	0
2 → 1	44 376.00 (+0.28)		43 060.24 (+0.23)		2.6	3.6	0	0
1 → 2	44 429.74 (+0.06)	44 441.68	43 104.18 (-0.04)	43 114.6	6.5	3.2	0	0
2 → 2	44 564.10 (-0.11)		43 215.84 (+0.20)		6.5	3.6	0	0
2 ₁₂ → 3 ₀₈								
F = 0 → 1	13 852.05 (+0.05)		15 131.8 (+0.20)		0	0	0	0
1 → 2	13 858.45 (+0.01)	13 920.8	15 136.9 (+0.09)	15 188.55	0.98	0	0	0
2 → 3	13 894.5 (-0.11)		15 166.8 (-0.44)		1.54	0	0	0
3 → 4	13 953.6 (+0.05)		15 215.3 (+0.15)		1.35	0	0	0
4 → 5	14 231.6 (+0.22)		15 486.3 (+0.23)		0	0	0	-1.3
3 → 4	14 246.7 (+0.24)	14 241.7	15 499.2 (+0.11)	15 494.78	-1.35	0	0	+0.1
2 → 3	14 256.4 (+0.00)		15 507.4 (-0.07)		-1.54	0	0	+1.2
1 → 2	14 262.5 (-0.46)		15 512.4 (-0.27)		-0.98	0	0	+1.9
3 ₀₈ → 3 ₁₂								
F = 5 → 5	47 697.2 (+0.03)		46 503.6 (-0.09)		0	0	0.4	0
4 → 4	47 739.8 (+0.01)	47 737.9	46 539.0 (-0.25)	46 537.28	-3.64	-1.35	0.0	0
3 → 3	47 764.6 (+0.19)		46 560.0 (-0.09)		-3.75	-1.54	-0.3	0
2 → 2	47 778.2 (+0.05)		46 571.0 (+0.43)		-2.03	-0.98	-0.5	0
1 → 1	48 232.10 (-0.42)		47 037.0 (+0.18)		0	0	-1.9	0
2 → 2	48 276.60 (+0.28)	48 332.2	47 074.4 (-0.17)	47 120.44	2.03	0.98	-1.2	0
3 → 3	48 336.0 (+0.05)		47 122.6 (+0.28)		3.75	1.54	-0.1	0
4 → 4	48 398.20 (-0.17)		47 175.7 (-0.70)		3.64	1.35	1.3	0
5 ₁₄ → 4 ₂₈								
F = 4 → 3	25 261.0 (-0.13)		21 226.3 (+0.01)		-0.69	-1.81	0.9	-0.4
5 → 4	25 274.6 (+0.06)	25 286.4	21 237.5 (+0.15)	21 247.53	-0.86	-2.88	0.5	-0.2
6 → 5	25 290.1 (-0.05)		21 250.4 (-0.03)		-0.78	-2.53	-0.1	0.1
7 → 6	25 306.7 (-0.17)		21 264.3 (-0.13)		0	0	-0.8	0.4
6 → 5	25 798.5 (-0.08)		21 739.2 (-0.06)		0.78	2.53	1.1	0.8
5 → 4	25 828.1 (+0.40)	25 830.9	21 764.2 (+0.12)	21 765.92	0.86	2.88	0.1	0.1
4 → 3	25 852.7 (+0.01)		21 784.1 (+0.12)		0.69	1.81	-0.7	-0.5
3 → 2	25 870.1 (-0.11)		21 797.7 (+0.52)		0	0	-1.4	-1.0
6 ₂₆ → 7 ₁₆								
F = 4 → 5	20 688.0 (-0.15)		24 856.0 (-0.44)		0	0	-0.6	-0.7
5 → 6	20 713.3 (+0.09)	20 733.6	24 876.8 (-0.45)	24 893.26	1.44	0.4	-0.3	-0.4
6 → 7	20 741.8 (-0.12)		24 898.5 (+1.06)		2.18	0.7	0.1	0.1
7 → 8	20 770.6 (+0.18)		24 924.6 (-0.53)		1.85	0.6	0.5	0.6
8 → 9	20 857.2 (-0.20)		25 006.3 (-0.50)		0	0	0.3	-0.4
7 → 8	20 881.2 (+0.20)	20 885.7	25 026.1 (-0.30)	25 029.34	-1.85	-0.6	-0.0	-0.1
6 → 7	20 900.6 (-0.10)		25 041.0 (+0.70)		-2.18	-0.7	-0.2	0.2
5 → 6	20 915.9 (-0.40)		25 054.7 (-0.40)		-1.44	-0.4	-0.4	0.5
Σ[ν(calc) - ν(obs)] ² = 2.6 (Mc/sec) ²			Σ[ν(calc) - ν(obs)] ² = 5.1 (Mc/sec) ²					

^a $\nu(\text{calc}) - \nu(\text{obs})$ in parentheses after $\nu(\text{obs})$.^b $\epsilon, \epsilon', \epsilon, \epsilon'$ defined in text.

TABLE II. Fit of spin-rotation splitting of chlorine dioxide.

	Cl ³⁵ O ₂		Cl ³⁷ O ₂	
	($\nu_+ - \nu_-$) _{obs} ^a (Mc/sec)	$\Delta\nu_{\pm}$ ^b correction (Mc/sec)	($\nu_+ - \nu_-$) _{obs} ^a (Mc/sec)	$\Delta\nu_{\pm}$ ^b correction (Mc/sec)
ΔE_{101}	-159.0 (-0.02)	0.0	-158.9 (-0.07)	0.0
ΔE_{110}	-1211.4 (-0.04)	7.5	-1184.0 (+0.08)	7.1
$2_{12} \rightarrow 3_{03}$	320.9 (+0.39)	-14.9	306.2 (-0.09)	-14.1
$3_{03} \rightarrow 3_{12}$	-594.3 (+0.58)	11.7	-583.2 (-0.03)	11.1
$5_{14} \rightarrow 4_{23}$	-544.5 (-0.54)	23.0	-518.4 (-0.20)	22.2
$6_{25} \rightarrow 7_{16}$	152.1 (-0.85)	-18.9	136.1 (-0.12)	-17.5
	$\Sigma[(\text{calc}) - (\text{obs})]^2 = 1.50 \text{ (Mc/sec)}^2$		$\Sigma[(\text{calc}) - (\text{obs})]^2 = 0.08 \text{ (Mc/sec)}^2$	

^a ($\nu_+ - \nu_-$)_{calc} - ($\nu_+ - \nu_-$)_{obs} in parentheses.^b $\Delta\nu_{\pm}(\text{corr})$ is added to ($\nu_+ - \nu_-$)_{obs} to remove effect of second-order terms.

The J scheme would be a good choice of basis if the spin-rotation interaction were the largest, the E scheme if the quadrupole interaction were largest, and the G scheme if the Fermi interaction were the largest.

In the case of ClO₂ a rotational transition for large N should consist of two quartets if the J scheme is applicable, 4 doublets if the E scheme is applicable, and a group of 8 lines if the G scheme is applicable. Since the observed spectrum consisted of quartets the J scheme basis was naturally chosen.

For the J scheme basis the energy of a single hyperfine level can be represented to second-order perturbation by

$$E[N\tau JF] = \langle N\tau JF | H | N\tau JF \rangle + \frac{|\langle N\tau JF | H | N\tau(J\pm 1)F \rangle|^2}{E[N\tau JF] - E[N\tau(J\pm 1)F]} + \sum_{N'\tau'J'} \frac{|\langle N\tau JF | H | N'\tau'J'F \rangle|^2}{E[N\tau JF] - E[N'\tau'J'F]} (1 - \delta_{NN'}\delta_{\tau\tau'}), \quad (4)$$

where the quantity τ is the asymmetric rotor quantum number.

Complete evaluation of the sum over $N'\tau'$ is tedious since there are nonzero matrix elements for $\Delta N \leq 2$. Fortunately for the parameters found for ClO₂, it can be easily shown that there is only one term in the sum over $N'\tau'$ which contributes significantly. This term has $J' = J$, $K_{-1}' = K_{-1}$ (K_{-1} is the prolate-top K , $\tau = K_{-1} - K_{+1}$), and $\Delta N = \pm 1$ (\pm chosen in order to make $J' = J$).

Matrix elements of the terms in H for which $\Delta N = 0$ and $\Delta\tau = 0$ have been given previously.²⁻⁴ The required matrix elements for which $\Delta N = \pm 1$ are given in the Appendix for $\kappa = -1$. The effect of rotational asymmetry was not included for these terms.

$$\epsilon = \frac{|\langle N\tau JF | H | N\tau(J\pm 1)F \rangle|^2}{E[N\tau JF] - E[N\tau(J\pm 1)F]},$$

$$e = \frac{2\langle NK_{-1}\gamma J | H_{SR} | (N\pm 1)K_{-1}\gamma J \rangle \langle (N\pm 1)K_{-1}\gamma JF | H_D | NK_{-1}\gamma JF \rangle}{E[NK_{-1}\gamma J] - E[(N\pm 1)K_{-1}\gamma J]},$$

FITTING THE SPECTRUM

The spectra of Cl³⁵O₂ and Cl³⁷O₂ were fitted as follows: First the parameters were estimated and the second-order perturbation terms which depend on the subscript I and Q parameters were calculated. These were subtracted from the observed spectrum. Then the differences were fitted by least squares with $(0)_I$, $(aa)_I$, $(cc)_I$, $(aa)_Q$, $(cc)_Q$, and ν_{\pm} for the center of each quartet. In the case of the $1_{01} \rightarrow 1_{10}$ transition, $\nu_+(\frac{3}{2} - \frac{3}{2})$, $\nu_-(\frac{1}{2} - \frac{1}{2})$, and $\Delta E_{101}(\frac{3}{2} - \frac{1}{2})$ were used. The frequencies being fitted are linear functions of the parameters. The least-squares computation was carried out on the Rice University digital computer.

The spin-rotation interaction parameters were fitted to the $(\nu_+ - \nu_-)$ differences by the following procedure. The estimated values of $(aa)_S$, $(bb)_S$, and $(cc)_S$ were used to correct the differences between the ν_{\pm} 's by removing the second-order terms. The corrected differences between the ν_{\pm} 's were then fitted by least squares with $(0)_S$, $(aa)_S$, $(bb)_S$, and $(cc)_S$. The average of the two ν_{\pm} 's associated with a rotational transition was then corrected by the subscript S parameters obtained and the second-order perturbation terms, giving the hypothetical rotor frequency ν_0 for each transition. The rotational constants were fitted to the five ν_0 's by least squares. The transitions with $N \leq 3$ were given weight ten; the $5_{14} \rightarrow 4_{23}$, weight one; the $6_{25} \rightarrow 7_{16}$, weight one-half.

The new parameters obtained were used to recalculate the second-order perturbation terms. These were subtracted from the observed frequencies, and the least-squares fits were repeated. The parameters changed only very slightly.

Table I gives results of this second iteration for the two species. The observed frequencies which were reported in I are listed here again for convenience. The quantities ϵ' , ϵ , e' , and e are defined by

TABLE III. Rotational frequencies and constants of chlorine dioxide.

	Corrected ^a		$(\nu_+ + \nu_-)/2$ (Mc/sec)	$\Delta\nu(\text{corr})^b$ (Mc/sec)	ν_0^c (Mc/sec)	
	ν_+ (Mc/sec)	ν_- (Mc/sec)				
			Cl ³⁵ O ₂			
$1_{01} \rightarrow 1_{10}$	43 396.8	44 441.7	43 919.3	-174.3	43 745.0	(-0.25)
$2_{12} \rightarrow 3_{03}$	14 234.3	13 928.3	14 081.3	+40.6	14 121.9	(+0.12)
$3_{03} \rightarrow 3_{12}$	47 742.2	48 324.8	48 033.5	-41.3	47 992.2	(+0.13)
$5_{14} \rightarrow 4_{23}$	25 298.2	25 819.7	25 559.0	-40.3	25 518.7	(+10.9)
$6_{25} \rightarrow 7_{16}$	20 876.3	20 743.1	20 809.7	+12.0	20 821.7	(+11.2)
			Cl ³⁷ O ₂			
$1_{01} \rightarrow 1_{10}$	42 096.6	43 114.6	42 605.6	-169.7	42 435.9	(-0.30)
$2_{12} \rightarrow 3_{03}$	15 487.8	15 195.6	15 341.7	+39.3	15 381.0	(+0.14)
$3_{03} \rightarrow 3_{12}$	46 541.4	47 113.4	46 827.4	-40.9	46 786.5	(+0.16)
$5_{14} \rightarrow 4_{23}$	21 259.1	21 755.3	21 507.2	-38.7	21 468.5	(+11.2)
$6_{25} \rightarrow 7_{16}$	25 020.5	24 902.0	24 961.3	+11.4	24 972.7	(+8.0)

^a The ν_+ and ν_- frequencies given in Table I have been corrected for the effect of the spin-rotation Hamiltonian which is off-diagonal in N .

^b $\Delta\nu(\text{corr}) = [1/4(2N'+1)]\Sigma s' - [1/4(2N+1)]\Sigma s$, and is part of the correction mentioned in I.

^c ν_0 is the hypothetical rotor frequency. The numbers in parentheses are $[\nu(\text{calc}) - \nu(\text{obs})]$ where $\nu(\text{calc})$ is obtained from the parameters given in Table IV.

where

$$H_{\text{SR}} = (aa)_s N_a S_a + (bb)_s N_b S_b + (cc)_s N_c S_c,$$

$$H_D = (aa)_I I_a S_a + (bb)_I I_b S_b + (cc)_I I_c S_c;$$

γ is the asymmetric rotor quantum number which appears in the Wang wave function (see Appendix), ϵ' and e' refer to the upper state involved in the transition; ϵ and e refer to the lower state. Thus

$$\nu^* = \nu(\text{obs}) - \epsilon' + \epsilon - e' + e$$

should be a linear function of the parameters.

In Table II are listed the second iteration $\nu_+ - \nu_-$, $\Delta\nu(\text{corr})$ (the correction for second-order perturbation with other rotational levels), and the difference between the calculated and observed $\nu_+ - \nu_-$.

In Table III are listed ν_+ and ν_- corrected for second-order terms, $(\nu_+ + \nu_-)/2$, $\Delta\nu(\text{corr})$, ν_0 (the rotor frequency), and $\nu_0(\text{calc})$. In Table IV are listed all the parameters obtained in the fitting process.

The particular method of fitting used here was chosen for a number of reasons. First, it was decided that the

TABLE IV. Hamiltonian parameters obtained by fitting microwave spectrum of chlorine dioxide.

Cl^{35}O_2 (Mc/sec)	Cl^{37}O_2 (Mc/sec)	Ratio $\text{Cl}^{35}\text{O}_2 : \text{Cl}^{37}\text{O}_2$
$A = 52\,077.95$	$50\,733.98$	
$B = 9952.42$	9952.91	
$C = 8333.21$	8298.38	
$(0)_s = -533.6$	-521.4	
$(aa)_s = -855.0$	-830.9	
$(bb)_s = 316.9$	304.7	
$(cc)_s = 538.1$	526.2	
$(0)_I = 46.21$	38.48	1.201
$(aa)_I = -77.87$	-64.87	1.200
$(bb)_I = -83.09$	-69.02	$\mu_{35}/\mu_{37} = 1.201$
$(cc)_I = 160.96$	133.89	
$(aa)_Q = -8.65$	-6.82	1.268
$(bb)_Q = 0.38$	0.44	$Q_{35}/Q_{37} = 1.269$
$(cc)_Q = 8.27$	6.38	

spacings inside quartets would be most accurately represented by the equations used and approximations made. However, if one fitted the frequency differences in quartets, the experimentally observed lines would have different weights; by fitting ν_{\pm} to each quartet the experimental observations are weighted equally.

TABLE V. Predicted rotational constants and some observed microwave transitions of $\text{Cl}^{35}\text{O}^{16}\text{O}^{18}$. $A = 50\,578$ Mc/sec, $B = 9380$ Mc/sec, and $C = 7892$ Mc/sec.

	(Mc/sec)	$\Delta\nu(\text{corr})$ (Mc/sec)	$\nu_0(\text{obs})$ (Mc/sec)	$\nu_0(\text{calc})$ (Mc/sec)
$2_{12} \rightarrow 3_{03}$				
$F = 0 \rightarrow 1$	11 633.8(vvv)			
$1 \rightarrow 2$	11 640.1			
$2 \rightarrow 3$	11 677.5			
$3 \rightarrow 4$	11 736.2			
		55	11 905	11 906
$4 \rightarrow 5$	12 011.4			
$3 \rightarrow 4$	12 026.6			
$2 \rightarrow 3$	12 036.7 ^a			
$1 \rightarrow 2$	12 042.7			
$5_{14} \rightarrow 4_{23}$				
$F = 4 \rightarrow 3$	28 308.2			
$5 \rightarrow 4$	28 322.1			
$6 \rightarrow 5$	28 337.4			
$7 \rightarrow 6$	28 354.2			
		-45	28 562	28 567
$6 \rightarrow 5$	28 843.6			
$5 \rightarrow 4$	28 873.7			
$4 \rightarrow 3$	28 897.9			
$3 \rightarrow 2$	28 915.8 ^a			
$6_{25} \rightarrow 7_{16}$				
$F = 4 \rightarrow 5$	14 855.6			
$5 \rightarrow 6$	14 881.2			
$6 \rightarrow 7$	14 910.0			
$7 \rightarrow 8$	14 939.1			
		15	14 997	15 014
$8 \rightarrow 9$	15 035 ^a			
$7 \rightarrow 8$	15 059.2			
$6 \rightarrow 7$	15 078.4			
$5 \rightarrow 6$	15 093.6			

^a A normal line falls at this frequency, therefore one cannot be sure an O^{18} line is present.

TABLE VI. Comparison of frequency differences between corresponding hyperfine components of Cl³⁵O₂¹⁶ and Cl³⁵O¹⁶O¹⁸.

	$\Delta\nu(\text{O}^{18})$	$\Delta\nu(\text{O}^{16})$
$2_{12} \rightarrow 3_{03}$		
$F=0 \rightarrow 1$		
	6.3	6.4
$1 \rightarrow 2$	37.4	36.0
$2 \rightarrow 3$	58.7	59.1
$3 \rightarrow 4$	275.2	278.0
$4 \rightarrow 5$	15.2	15.1
$3 \rightarrow 4$	10.1	9.7
$2 \rightarrow 3$	6.0	6.1
$1 \rightarrow 2$		
$5_{14} \rightarrow 4_{23}$		
$F=4 \rightarrow 3$		
	13.9	13.6
$5 \rightarrow 4$	15.3	15.5
$6 \rightarrow 5$	16.8	16.6
$7 \rightarrow 6$	489.4	491.8
$6 \rightarrow 5$	30.1	29.6
$5 \rightarrow 4$	24.2	24.6
$4 \rightarrow 3$	17.9	17.4
$3 \rightarrow 2$		
$6_{25} \rightarrow 7_{16}$		
$F=4 \rightarrow 5$		
	25.6	25.3
$5 \rightarrow 6$	28.8	28.5
$6 \rightarrow 7$	29.1	28.8
$7 \rightarrow 8$	96.	86.6
$8 \rightarrow 9$	24.	24.0
$7 \rightarrow 8$	19.2	19.4
$6 \rightarrow 7$	15.2	15.3
$5 \rightarrow 6$		

The reason it was decided that $\nu_+ - \nu_-$ would not be as accurately fitted is that $\Delta\nu(\text{corr})$ was calculated for $\kappa = -1$ and the magnitude of the error incurred by this approximation should increase with N . In order to estimate this error, $\Delta\nu(\text{corr})$ arising from $6_{25} \leftrightarrow 7_{25}$ has been calculated for $\kappa = -0.9259$ and is found to be -11.9 Mc/sec compared to -11.2 for $\kappa = -1$.

Finally, the rotor frequencies were not expected to be exactly fitted because of centrifugal distortion.

MICROWAVE SPECTRUM OF Cl³⁵O¹⁶O¹⁸

A sample of O¹⁸-ClO₂ was prepared as follows. Sodium hydride (0.3 g) was dissolved in a fivefold excess of 30% O¹⁸-H₂O. Then Cl₂ gas was passed through the solution, giving NaClO₃ and NaCl. The NaClO₃ was made to react with oxalic acid to give O¹⁸ chlorine dioxide.

The rotational constants of Cl³⁵O¹⁶O¹⁸ were predicted from the structure of chlorine dioxide and Kraitichmann's equations, and are given in Table V. From these the ν_0 's of several rotational transitions were predicted. The observed ν_0 's are compared to the predicted ν_0 's in Table V. This comparison confirms the rotational assignment. The approach used and the $\Delta\nu(\text{corr})$ given are the same as those of paper I.

The most conclusive confirmation of the rotational assignment of Cl³⁵O¹⁶O¹⁸ is obtained by comparison of the frequency differences between successive hyperfine components of the O¹⁸ transitions with the frequency differences between the corresponding components of the corresponding O¹⁶ transitions. These comparisons are shown in Table VI.

The close correspondence of the spacings inside quartets indicates that the subscript I parameters and the subscript Q parameters are unchanged to our experimental accuracy by O¹⁸ substitution. However, the splitting between quartets is changed by a few megacycles per second by O¹⁸ substitution. Therefore, the three subscript S parameters were fitted to the three $\nu_+ - \nu_-$ in Table VII.

The rotational constants A , B , and C were fitted to the three ν_0 's in Table VIII assuming the same apparent centrifugal distortion as in Cl³⁵O₂¹⁶. The very slightly revised structure obtained for ClO₂ is also given in Table VIII. This is now an r_s structure.

DISCUSSION AND INTERPRETATION OF HYPERFINE PARAMETERS OBTAINED

The first item to be considered is the internal consistency of the hyperfine parameters obtained for the various isotopes. The subscript- I parameters should be proportional to the magnetic moment of the Cl nucleus.

TABLE VII. Spin-rotation interaction of Cl³⁵O¹⁶O¹⁸.

	$(\nu_+ - \nu_-)_{\text{obs}}$ (Mc/sec)	$\Delta\nu_{\text{corr}}^a$ (Mc/sec)
$2_{12} \rightarrow 3_{03}$	318.8	-15.2
$5_{14} \rightarrow 4_{23}$	-542.5	23.6
$6_{25} \rightarrow 7_{16}$	161.9	-19.3
$(aa)_S$	-828.5	
$(bb)_S$	310.9	
$(cc)_S$	517.6	
$(0)_S$	-513.3	

^a $\Delta\nu(\text{corr})$ arises from second-order perturbation off diagonal in N and must be added to $(\nu_+ - \nu_-)_{\text{obs}}$ to remove these terms.

TABLE VIII. Calculation of the rotational constants of $\text{Cl}^{35}\text{O}^{16}\text{O}^{18}$ and the r_s structure of ClO_2 .

	ν_+ (Mc/sec)	ν_- (Mc/sec)	$(\nu_+ + \nu_-)/2$ (Mc/sec)	$\Delta\nu(\text{corr})^a$ (Mc/sec)	ν_0 (Mc/sec)	$\Delta\nu_0^b$ (Mc/sec)	ν_0 corrected (Mc/sec)
$2_{12} \rightarrow 3_{03}$	12 021.8	11 703.0	11 862.4	40.0	11 902.4	0.0	11 902.4
$5_{14} \rightarrow 4_{23}$	28 333.8	28 876.2	28 605.0	-39.2	28 565.8	10.9	28 576.7
$6_{25} \rightarrow 7_{16}$	15 063.6	14 901.7	14 982.65	11.8	14 994.4	11.2	15 005.6
	$A = 50\,580.9$ (Mc/sec)				$r_s = 1.471$ Å		
	$B = 9379.6$ (Mc/sec)				$(\text{OClO})_s = 117^\circ 35'$		
	$C = 7891.7$ (Mc/sec)						

^a $\Delta\nu(\text{corr})$ includes 2nd order effects off diagonal in N and the $\Delta\nu(\text{corr})$ of Table III.^b $\Delta\nu_0$ is added to ν_0 to obtain $\nu_0(\text{corrected})$. It removes the apparent centrifugal distortion found in $\text{Cl}^{35}(\text{O}^{16})_2$.

The subscript- Q parameters should be proportional to the electric quadrupole moment of the Cl nucleus. Therefore, these parameters should be the same for the two Cl^{35} species, $\text{Cl}^{35}\text{O}_2^{16}$ and $\text{Cl}^{35}\text{O}^{16}\text{O}^{18}$. Since quartet spacings of corresponding transitions are identical, this criterion is satisfied.

TABLE IX. Effect of isotopic substitution on spin-rotation parameters.

	$\text{Cl}^{35}(\text{O}^{16})_2$	$\text{Cl}^{37}(\text{O}^{16})_2$	$\text{Cl}^{35}\text{O}^{16}\text{O}^{18}$
A_s	-1388.7	-1352.3	-1341.8
B_s	-216.6	-216.7	-202.4
C_s	4.6	4.6	4.3
A_s^{35}/A_s	...	1.026	1.030
A_s^{35}/A_s	...	1.026	1.034
B_s^{35}/B_s	...	1.000	1.061
B_s^{35}/B_s	...	1.000	1.071

The ratios of these parameters for Cl^{35}O_2 to Cl^{37}O_2 are given in Table IV. Also, the ratios of the magnetic and quadrupole moments are given. The agreement is highly satisfactory.

The quantities A_s , B_s , C_s , which are defined as $A_s = (aa)_s + (0)_s$, $B_s = (bb)_s + (0)_s$, etc., should be proportional to the corresponding rotational constant.⁵ The proportionality constant should be nearly independent of isotopic substitution. In Table IX these parameters are compared for the different isotopic species analyzed. The isotope dependence agrees well with that of the rotational constant.

ACKNOWLEDGMENTS

The help of James Church and of the Rice Computer Staff with the numerical calculations is gratefully acknowledged.

APPENDIX

Matrix Elements Off-Diagonal in N , τ , used in Fitting the Spectrum

The asymmetric rotor notation used here is N , K_{-1} , and γ , where

$$\psi(NK_{-1}\gamma) = (2)^{-1}[\psi(NK_{-1}) + (-1)^\gamma\psi(N-K_{-1})]$$

and $\psi(NK_{-1})$ is the wave function for the prolate symmetric top. In the formulas given below, $\kappa = -1$.

$$\langle (N+1)K_{-1}\gamma'JF | H_{\text{SR}} | NK_{-1}\gamma JF \rangle = \frac{-3K[(N+1)^2 - K^2]^{\frac{1}{2}}\{(aa)_s + \frac{1}{6}\delta_{1K}(-1)^{N+1}(N+1)[2(cc)_s + (aa)_s]\}}{4(N+1)}, \quad (1)$$

where H_{SR} is the spin-rotation interaction. For B_s levels, the δ_{1K} terms have opposite signs.

$$\begin{aligned} \langle (N+1)K_{-1}\gamma'JF | H_D | NK_{-1}\gamma JF \rangle \\ = \frac{[J(J+1) + I(I+1) - F(F+1)]3K[(N+1)^2 - K^2]^{\frac{1}{2}}\{(aa)_I + \frac{1}{6}\delta_{1K}(-1)^{N+1}(N+1)[2(cc)_I + (aa)_I]\}}{2(2N+1)(2N+3)(N+1)}, \quad (2) \end{aligned}$$

where H_D is the magnetic dipole-dipole interaction between the nuclear and electronic spin.

⁵ J. H. Van Vleck, Revs. Modern Phys. **23**, 213 (1951).

These matrix elements are used in the calculation of the second-order perturbation corrections e and $\Delta\nu_{\pm}(\text{corr})$.

$$e = \frac{2\langle(N+1)K_{-1}\gamma JF|H_{\text{SR}}|NK_{-1}\gamma JF\rangle\langle NK_{-1}\gamma JF|H_{\text{D}}|(N+1)K_{-1}\gamma JF\rangle}{E[NK_{-1}\gamma JF] - E[(N+1)K_{-1}\gamma JF]}. \quad (3)$$

$$\Delta\nu_{\pm}(\text{corr}) = -\Delta E_+' + \Delta E_-' + \Delta E_+ - \Delta E_-, \quad (4)$$

where

$$\Delta E_+ = \frac{|\langle(N+1)K_{-1}\gamma JF|H_{\text{SR}}|NK_{-1}\gamma JF\rangle|^2}{E[NK_{-1}\gamma JF] - E[(N+1)K_{-1}\gamma JF]},$$

$$\Delta E_- = \frac{|\langle NK_{-1}\gamma JF|H_{\text{SR}}|(N-1)K_{-1}\gamma JF\rangle|^2}{E[NK_{-1}\gamma JF] - E[(N-1)K_{-1}\gamma JF]}.$$