Investigation of the Microwave Spectrum of Perchlorylfluoride by Microwave Fourier Transform Spectroscopy

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We reinvestigated the rotational spectrum of perchlorylfluoride-^{35}Cl and -^{37}Cl by microwave Fourier transform spectroscopy and determined the rotational, centrifugal and quadrupole coupling constants and the dipole moment with higher precision and the spin-rotation constants for the first time.

Introduction

The infrared (IR) and microwave (MW) spectrum of perchlorylfluoride, $FClO_3$, have been the subject of a number of publications. The chlorine fluorine and chlorine oxygen bonds are of interest. Lide and Mann [1] investigated the IR spectrum with the rather sure conclusion that the molecule has C_{3v} point symmetry. The first successful observation of the MW spectrum was reported by Lide [2] after an unsuccessful attempt [3]. After some estimates for the dipole moment [4, 5] DeLeon and Muenter [6] determined the dipole moment by a molecular beam experiment.

Experimental

We used our microwave Fourier transform (MWFT) spectrometers in the region from 10 to 32 GHz [7–10] to investigate the rotational spectrum up to the angular momentum quantum number $J=3$ with $K=0$. Transitions with $J=3$ and $K\geqq 0$ are outside the frequency range of our instruments. It should be mentioned that spin statistics [11] under the assumption of C_{3v} symmetry of the molecule does not allow levels with $K \neq 3n$, $n=0, \pm 1, \pm 2, \ldots$.

The assignment of the lines with $J=1-0$, $2-1$, $3-2$ and $K=0$ was straightforward with the reported data [2]. We found no features which can be attributed to $K=1$ or $K=2$ transitions. So the assumption of C_{3v} symmetry seems to be justified.

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The measurements were made at a pressure of approximately 3 mTorr (0.4 Pa) and approximately -50 °C. The spectra are given in Tables 1 to 3 for $F^{35}ClO_3$ and $F^{37}ClO_3$. The frequencies of components in narrow multiplets were determined by a fitting procedure [12] of the time domain signal. Figure 1 gives an example.

The substance was prepared by the reaction [13]

$$KClO_4 + HSO_3F \rightarrow FClO_3 + KHSO_4 .$$

Analysis

We analysed the spectra by the model of a centrifugal distorted symmetric top [14] supplemented by quadrupole [15] and chlorine spin-rotation [16] coupling by our program SYM2QS.FOR. The

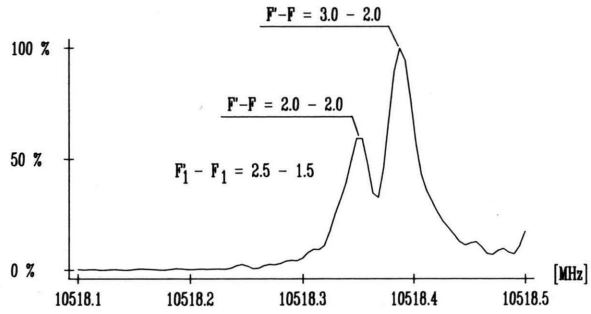

Fig. 1. Quadrupole hyperfine components $F'_1 - F_1 = 5/2 - 3/2$ of the transition $J'-J=1-0$ showing an additional splitting interpreted as fluorine spin-rotation coupling. F overall angular momentum quantum number. -50 °C, 3 mTorr (0.4 Pa), polarisation frequency 10 518.5 MHz, sample interval 50 ns, 1024 data points supplemented by 3072 zeroes before Fourier transformation, 10 600 K experiment cycles.

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Table 1. Observed and calculated frequencies of quadrupole hyperfine structure of $F^{35}ClO_3$; only $K=0$ transitions exist, $\Delta\nu=\nu_{obs}-\nu_{calc}$, * not resolvable hyperfine components.

$J'-J$	$F'-F$	ν_{obs}/MHz	ν_{calc}/MHz	$\Delta\nu$/kHz
1–0	2.5–1.5	10 518.362	10 518.364	−2
	1.5–1.5	10 513.445	10 513.445	0
	0.5–1.5	10 522.286	10 522.283	3
2–1	3.5–2.5	21 035.149	21 035.146	3
	2.5–1.5	*	21 035.143	6
	2.5–2.5	21 030.223	21 030.225	−2
	1.5–1.5	21 038.646	21 038.646	0
	1.5–0.5	21 029.804	21 029.808	−4
	0.5–0.5	21 034.714	21 034.715	−1
3–2	4.5–3.5	31 552.233	31 552.236	−3
	3.5–2.5	*	31 552.234	1
	3.5–3.5	31 547.317	31 547.312	5
	2.5–2.5	31 554.507	31 554.516	−9
	2.5–1.5	31 551.016	31 551.014	2
	1.5–0.5	*	31 551.012	4
	1.5–1.5	31 555.920	31 555.919	1

Table 2. Observed and calculated frequencies of the $J'-J=1-0$ transition used for the analysis of the fluorine spin-rotation coupling of $F^{35}ClO_3$. The error of ν_{obs} results from averaging several measurements with different polarisation frequencies. It does not include systematic errors.

$F_1'-F_1$	$F'-F$	ν_{obs}/MHz	ν_{calc}/MHz	$\Delta\nu$/kHz
2.5–1.5	3.0–2.0	10 518.3788(2)	10 518.376	3
	2.0–2.0	10 518.3485(2)	10 518.349	1
1.5–1.5	2.0–2.0	10 513.4455(6)	10 513.446	0
	1.0–1.0	10 513.4316(6)	10 513.434	−2
0.5–1.5	0.0–1.0	10 522.2938(9)	10 522.296	−2
	1.0–1.0	10 522.2807(4)	10 522.281	0

Table 3. Observed and calculated frequencies of quadrupole hyperfine structure of $F^{37}ClO_3$; only $K=0$ transitions exist. * not resolvable hyperfine components.

$J'-J$	$F'-F$	ν_{obs}/MHz	ν_{calc}/MHz	$\Delta\nu$/kHz
1–0	2.5–1.5	10 513.073	10 513.077	−4
	1.5–1.5	10 509.191	10 509.198	−7
	0.5–1.5	10 516.162	10 516.162	0
2–1	3.5–2.5	21 024.901	21 024.900	1
	2.5–1.5	*	21 024.897	4
	2.5–2.5	21 021.015	21 021.019	−4
	1.5–1.5	21 027.658	21 027.656	2
	1.5–0.5	21 020.706	21 020.692	14
	0.5–0.5	21 024.550	21 024.558	8
3–2	4.5–3.5	31 536.950	31 536.955	−5
	3.5–2.5	*	31 536.953	−2
	3.5–3.5	31 533.069	31 533.071	−2
	2.5–2.5	31 538.746	31 538.749	−3
	2.5–1.5	31 535.992	31 535.991	1
	1.5–0.5	*	31 535.988	4
	1.5–1.5	31 539.860	31 539.854	5

Table 4. Rotational, centrifugal, quadrupole coupling and spin-rotation coupling constants B, D_J, χ_{zz}, $C_N(Cl)$, $C_N(F)$ in MHz and the dipole moment μ in Debye for the isotope ^{35}Cl of perchlorylfluoride. The second column shows for comparison the results of Lide et al. [2] and DeLeon and Muenter [6].

	$F^{35}ClO_3$	$F^{35}ClO_3$	
B	5258.6913(7)	5258.682(5)	[2]
D_J	0.00139(4)	0.0014(2)	[2]
χ_{zz}	−19.647(7)	−19.2(5)	[2]
$C_N(Cl)$	0.0028(6)	–	
$C_N(F)$	0.0234(24)	–	
μ	0.02700(4)	0.0228(4)	[6]

Standard deviation of the fit [B, D_J, χ_{zz}, $C_N(Cl)$]: 4 kHz

Table 5. Rotational, centrifugal, quadrupole coupling and spin-rotation coupling constants B, D_J, χ_{zz}, $C_N(Cl)$ for the isotope ^{37}Cl of perchlorylfluoride in MHz. The second column shows for comparison the results of Lide et al. [2].

	$F^{37}ClO_3$	$F^{37}ClO_3$
B	5256.1516(10)	5256.149(5)
D_J	0.00132(7)	0.0014(2)
χ_{zz}	−15.484(10)	−15.4(15)
$C_N(Cl)$	0.0029(9)	–

Standard deviation of the fit: 6 kHz

Table 6. Observed and calculated frequencies of Stark satellites of the $J'-J=1-0$, $K=0$ rotational transition of (^{35}Cl)-perchlorylfluoride. E: Stark voltage, * not resolvable hyperfine components, ** not included in fit.

$F'-F$	M_F	E/V	ν_{obs}/MHz	ν_{calc}/MHz	$\Delta\nu$/kHz
2.5–1.5	1.5	1003.32	10 518.462	10 518.459	3
	0.5	*	*	10 518.474	−12**
	1.5	1500.79	10 518.570	10 518.577	−7
	0.5	*	*	10 518.610	40**
	1.5	2000.80	10 518.741	10 518.745	−3
	0.5	2000.80	10 518.805	10 518.799	6
	1.5	2500.66	10 518.974	10 518.963	11
	0.5	2500.66	10 519.041	10 519.039	2
	1.5	3001.00	10 519.231	10 519.235	−4
	0.5	3001.00	10 519.338	10 519.328	10
	1.5	3503.20	10 519.555	10 519.564	−9
	0.5	3503.20	10 519.658	10 519.665	−7
1.5–1.5	1.5	1008.24	10 513.552	10 513.557	−4
	1.5	2000.80	10 513.877	10 513.880	−3
	1.5	3003.80	10 514.399	10 514.411	−12
	1.5	3505.20	10 514.746	10 514.746	0
0.5–1.5	0.5	1000.88	10 522.396	10 522.372	24
	0.5	1500.50	10 522.493	10 522.483	10
	0.5	2004.40	10 522.656	10 522.644	12
	0.5	2500.56	10 522.853	10 522.850	3
	0.5	3001.90	10 523.122	10 522.109	13

Hamiltonian matrix was set up in the coupled basis $|J, K, I, F, M_F\rangle$ with matrix elements from [17] and diagonalised. The spin-rotation was included in first order. The results are given in Tables 4 and 5.

For the few lines of Table 2 we observed an additional splitting partly as shoulders. We interpreted this splitting as a fluorine spin-rotation interaction. This leads to a problem of plural coupling [18]. The value given in Table 4 for C_N(F) is a result of a first order treatment with the program SYM2QS.FOR in the coupled basis $|J, K, I_1(\text{Cl}), F_1, I_2(\text{F}), F, M_F\rangle$. Here the valus of B, D_J, χ_{zz}(Cl) and C_N(Cl) were fixed to the values given in the first four lines of Table 4, as we could measure only few lines showing this splitting.

We determined further the dipole moment using our MWFT spectrometer [19] with a Stark cell. The cell was calibrated against OCS with its dipole moment of 0.715196(10) D [20] giving a spacing of the septum from the wall of 0.25718(1) cm [21]. The Stark measurements are given in Table 6 for the $J=1-0$ transition for $F^{35}ClO_3$.

The data were analysed including the ^{35}Cl quadrupole coupling with our program L.FOR for a linear molecule as only $K=0$ transitions were observed. The Hamiltonian matrix given in [22], supplemented by the Cl spin-rotation contribution [23], was diagonalized. The result is also given in Table 4. For comparison we give values reported in [2] and [6].

It should be pointed out that the rotational constant B, the distortion constant D_J and the ^{35}Cl coupling constant χ_{zz} are more precise than in [2] and [6], but within the error limits of [2]. The dipole moment evaluated in [6] from the hfs transition $F=5/2-7/2$ of the $J=3$, $K=3$ level is $\mu=0.0228(4)$ D. It is different from our value $\mu=0.02700(4)$ D determined from the $J=1-0$, $K=0$ transition.

We doubt that the difference of the values stems from the variation of the dipole moment with the J and K values.

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