The Microwave Spectrum of 1,1-Dichloro-2,2,2-trifluoroethane

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We assigned the microwave spectrum of 1,1-dichloro-2,2,2-trifluoroethane in its vibrational ground state using a pulsed molecular beam microwave Fourier transform (MB-MWFT) spectrometer. For the ^{35}Cl,^{35}Cl-isotopomer the rotational constants were found to be $A = 2105.7098\,(38)$ MHz, $B = 1689.8304\,(35)$ MHz, and $C = 1135.6955\,(23)$ MHz, the quadrupole coupling constants of the ^{35}Cl-nuclei are $\chi_{aa} = 12.385\,(35)$ MHz and $\chi_{bb} = -42.284\,(31)$ MHz. The rotational constants of the ^{35}Cl,^{37}Cl-isotopomer are $A = 2071.5469\,(33)$ MHz, $B = 1670.7648\,(36)$ MHz, and $C = 1117.1755\,(24)$ MHz, the corresponding quadrupole coupling constants are $\chi_{aa} = 17.639\,(51)$ MHz and $\chi_{bb} = -47.670\,(67)$ MHz for the ^{35}Cl-nucleus and $\chi_{aa} = 4.701\,(54)$ MHz and $\chi_{bb} = -28.331\,(83)$ MHz for the ^{37}Cl-nucleus.

Introduction

In the course of our studies on halogenated alkanes we found 1,1-dichloro-2,2,2-trifluoroethane ($CHCl_2CF_3$) an interesting molecule, whose spectrum was to our knowledge unassigned. It is also of interest as a substitute for chlorofluorocarbons (CFC). Expecting a very dense spectrum crowded with many lines from highly excited rotational and vibrational states we decided to record the spectrum using our molecular beam microwave Fourier transform (MB-MWFT) spectrometer where, due to a very low rotational and also low vibrational temperature, such perturbations are usually avoided. Due to a very characteristic chlorine quadrupole hyperfine structure (hfs) the assignment turned out to be rather easy and was finally done in less than one week.

Experimental

All measurements were carried out using an MB-MWFT spectrometer [1] with automatic scanning facilities. A sample of 1–2% 1,1-dichloro-2,2,2-trifluoroethane in argon at a stagnation pressure of $5 \cdot 10^4$ Pa (0.5 atm) was used throughout. 1,1-Dichloro-2,2,2-trifluoroethane was obtained from Hoechst AG, Frankfurt.

Analysis

We started our experiments with a spectrum roughly predicted with rotational constants obtained from estimated structural parameters. A corresponding Fortrat diagram is given in Figure 1. The chlorine hfs was predicted with coupling constants adopted from molecules with similar nuclear environment. After scanning a total of 2 GHz at various areas between 7.5 and 14.2 GHz all lines were remeasured in the high resolution mode of the spectrometer and identified by

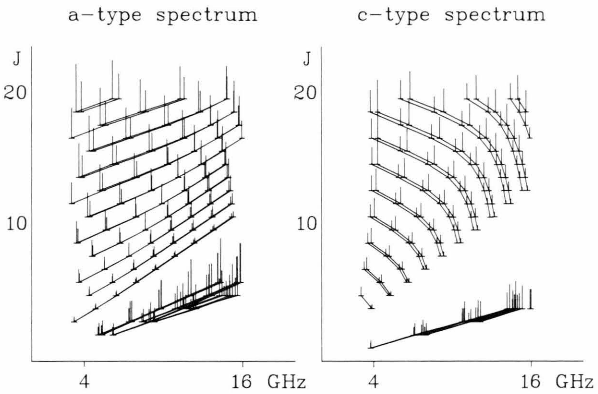

Fig. 1. Fortrat diagram showing transitions of ^{35}Cl,^{35}Cl- and ^{35}Cl,^{37}Cl-1,1-dichloro-2,2,2-trifluoroethane. Line strengths are indicated by vertical bars. Due to similar rotational constants the isotopomers appear as doublets with an intensity ratio of 3 : 2 according to a ratio of isotopic abundance of 3 : 1 and the equivalence of the ^{35}Cl,^{37}Cl- and ^{35}Cl,^{37}Cl-species. a- and c-type transitions are drawn in separate diagrams. Only those lines with J < 6 in the range from 7.5–14.5 GHz were observed.

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Table 1. List of 2 out of 12 measured transitions of ^{35}Cl,^{35}Cl-1,1-dichloro-2,2,2-trifluoroethane [2].

$J'' K_a'' K_c''$	rotational quantum numbers of the upper level;
$J' K_a' K_c'$	rotational quantum numbers of the lower level;
$F'' I''$	total and intermediate angular momentum quantum numbers of the upper level;
$F' I'$	total and intermediate angular momentum quantum numbers of the lower level;
obs	observed frequencies (in MHz) averaged over fluorine hfs;
obs-calc	observed-minus-calculated frequencies (in kHz).

$J'' K_a'' K_c''$ $J' K_a' K_c'$	$F'' I''$ $F' I'$	obs	obs-calc
3 2 2 2 1 2	4 3 − 3 3	11395.223	36
	3 0 − 2 0	11394.664	29
	5 3 − 4 3	11393.081	30
	2 1 − 1 1	11392.774	−6
	5 2 − 4 2	11386.626	−18
	4 1 − 3 1	11384.455	−54
	6 3 − 5 3	11382.348	−26
	3 2 − 2 2	11378.635	−19
	3 1 − 2 1	11378.138	35
	1 3 − 1 3	11376.231	−7
5 1 5 4 1 4	8 3 − 7 3	12088.757	8
	5 2 − 4 2	12088.512	2
	5 1 − 4 1	12088.492	0
	7 3 − 6 3	12088.046	7
	7 2 − 6 2	12087.665	4
	6 1 − 5 1	12087.463	2
	5 0 − 4 0	12086.811	−1
	4 1 − 3 1	12086.761	−4
	6 3 − 5 3	12086.739	−2
	4 3 − 3 3	12086.650	1
	3 3 − 2 3	12086.451	−12
	5 3 − 4 3	12086.004	−5

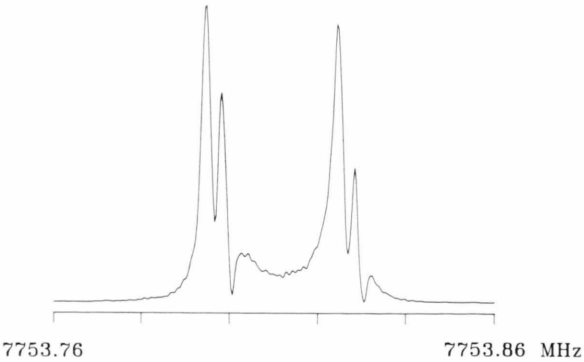

Fig. 2. The F, I: 5,3–4,3 component of the chlorine hyperfine pattern of the J, K_a, K_c: 2,2,0–1,1,0 transition. The main splitting of 29.8 kHz is caused by the Doppler effect corresponding to a beam velocity of 600 m/s parallel to the mirror axis, the triplet splitting is most probably due to fluorine spin rotation coupling. Recording conditions: polarizing pulses at 7753.810 MHz with 1 μs length and 0.3 mW pulse power, 100 ns sample interval, 8 k = 8192 data points, 8000 averaging cycles, stagnation pressure $5 \cdot 10^4$ Pa (0.5 atm).

Table 2. List of 2 out of 6 measured transitions [2] of ^{35}Cl,^{37}Cl-1,1-dichloro-2,2,2-trifluoroethane. For a list of symbols see Table 1.

$J'' K_a'' K_c''$ $J' K_a' K_c'$	$F'' I''$ $F' I'$	obs	obs-calc
3 2 2 2 1 2	4 3 − 3 3	11234.638	−2
	3 0 − 2 0	11234.150	1
	5 3 − 4 3	11232.788	7
	2 1 − 1 1	11232.498	−23
	4 1 − 3 2	11226.911	−30
	5 2 − 4 2	11226.866	14
	4 2 − 3 1	11224.960	−33
	6 3 − 5 3	11223.103	−6
	3 2 − 2 2	11220.152	1
	3 1 − 2 1	11218.893	33
	1 3 − 1 3	11217.567	37
5 0 5 4 0 4	8 3 − 7 3	11904.280	3
	5 2 − 4 2	11904.110	8
	5 1 − 4 1	11904.063	−11
	2 3 − 1 3	11903.642	−8
	7 3 − 6 3	11903.433	5
	7 2 − 6 2	11903.290	4
	6 1 − 5 1	11903.232	−2
	3 2 − 2 2	11903.160	−2
	6 2 − 5 2	11903.032	−0
	4 2 − 3 2	11902.957	6
	4 3 − 3 3	11902.608	1
	4 1 − 3 1	11902.339	−1
	5 0 − 4 0	11902.333	−1
	6 3 − 5 3	11902.257	0
	5 3 − 4 3	11901.664	−1

their hfs. A list of some selected frequencies [2] for both the ^{35}Cl,^{35}Cl and ^{35}Cl,^{37}Cl-isotopomer are presented in Tables 1 and 2, respectively. Since almost all hyperfine components were considerably broadened or even split by spin-rotation coupling of three fluorine nuclei, the center frequencies of the hyperfine components were estimated with an accuracy of about 10–20 kHz. This is considerably worse than the instrumental linewidth of 2 kHz (FWHH) [3]. A example is shown in Figure 2. In the case of the ^{37}Cl,^{37}Cl-species only a few line were observed in the scan and we decided to restrict our analysis to the two most abundant isotopomers.

The hfs was analyzed using the programs Q4 [4] and Q4FIT which perform first order calculations for two equivalent or nonequivalent nuclei in the $((I_1, I_2) I, J) F$ coupling scheme. A program for a more exact treatment by diagonalization of complete F blocks which would also allow for the determination of more than one off-diagonal element of the coupling tensor is under development [5] but not yet available. Therefore the observed-minus-calculated values are much larger than the experimental uncertainty. The

Table 3. Chlorine quadrupole coupling constants (in MHz) and standard errors of ^{35}Cl,^{35}Cl- and ^{35}Cl,^{37}Cl-1,1-dichloro-2,2,2-trifluoroethane.
N: Number of hyperfine components included in the fit.
σ: Standard deviation of the fit (in kHz).

	^{35}Cl,^{35}Cl	^{35}Cl,^{37}Cl
χ_{aa} (^{35}Cl)	12.385 (35)	17.639 (51)
χ_{bb} (^{35}Cl)	−42.284 (31)	−47.670 (67)
χ_{aa} (^{37}Cl)	–	4.701 (54)
χ_{bb} (^{37}Cl)	–	−28.331 (83)
N	128	92
σ	28	28

Table 4. Hyperfine free line centers of ^{35}Cl,^{35}Cl-1,1-dichloro-2,2,2-trifluoroethane.
$J'' K_a'' K_c''$ rotational quantum numbers of the upper level
$J' K_a' K_c'$ rotational quantum numbers of the lower level
obs observed frequencies (in GHz)
obs-calc observed-minus-calculated frequencies (in kHz)

$J'' K_a'' K_c''$	$J' K_a' K_c'$	obs	obs-calc
2 2 0	1 1 0	7.752759	35
2 2 1	1 1 1	8.006926	−34
3 1 2	2 0 2	10.854904	4
3 2 1	2 1 1	10.893115	55
3 2 2	2 1 2	11.386645	25
3 3 0	2 2 0	11.918323	−18
3 3 1	2 2 1	12.097708	−6
4 2 3	3 2 2	11.051161	−22
4 2 2	3 1 2	14.337595	−34
4 3 1	3 2 1	14.811258	−2
5 1 5	4 1 4	12.087661	3
5 0 5	4 0 4	12.095201	7

Table 5. Hyperfine free line centers of ^{35}Cl,^{37}Cl-1,1-dichloro-2,2,2-trifluoroethane. For a list of symbols see Table 4.

$J'' K_a'' K_c''$	$J' K_a' K_c'$	obs	obs-calc
3 1 2	2 0 2	10.722879	−21
3 2 1	2 1 1	10.747447	27
3 2 2	2 1 2	11.226942	7
3 3 0	2 2 0	11.730971	1
3 3 1	2 2 1	11.910424	−12
5 0 5	4 0 4	11.903219	−1

Table 6. Rotational constants (in MHz) and standard errors of ^{35}Cl,^{35}Cl- and ^{35}Cl,^{37}Cl-1,1-dichloro-2,2,2-trifluoroethane as obtained with program ZFAP4. Correlation matrices are also given.

	^{35}Cl,^{35}Cl			^{35}Cl,^{37}Cl		
A	2105.7098 (38)			2071.5469 (33)		
B	1689.8304 (35)			1670.7648 (36)		
C	1135.6955 (23)			1117.1755 (24)		
	Correlation coefficients					
A	1.000			1.000		
B	−0.580	1.000		−0.557	1.000	
C	−0.005	−0.136	1.000	−0.059	−0.023	1.000

Table 7. Assumed (a) and fitted (f) structural parameters. The agreement between observed and calculated rotational constants of both isotopomers is better than 0.1 MHz. A global C_s symmetry and a local C_{3v} symmetry at the CF_3 group were presupposed.

R (C–H)	109 pm (a)	∢ (C–C–H)	109.5° (a)
r (C–C)	154 pm (a)	∢ (C–C–F)	110.0° (a)
r (C–F)	133.6 pm (f)	∢ (C–C–Cl)	109.5° (a)
r (C–Cl)	177.5 pm (f)	∢ (Cl–C–Cl)	110.11° (f)

coupling constants of both isotopomers are compiled in Table 3.

With the hypothetical center frequencies (Table 4 and Table 5) of the hyperfine patterns we fitted the three rotational constants of both isotopomers using program ZFAP4 [6]. Due to the limited number of transitions no attempt was made to fit centrifugal distortion constants. The results are given in Table 6.

Discussion

The rotational constants of 1,1-dichloro-2,2,2-trifluoroethane were used to fit some of its structural parameters. Therefore a global C_s symmetry of the molecule and a local C_{3v} symmetry for the CF_3 group were presupposed. Due to a lack of sufficient data we decided to fix the C–C and the C–H bond distances and the C–C–H, C–C–F, and C–C–Cl angles at reasonable values. The C–Cl and C–F distances and the Cl–C–Cl angle resulting from the fit are fully compatible with the structural data of similar molecules like CF_3–CCl_3 and CH_3–$CHCl_2$. The assumed and fitted structural parameters are summarized in Table 7. Using these data the rotational constants of both isotopomers are reproduced within less than 0.1 MHz.

The quadrupole coupling constants are well determined but less accurate than it is usually expected when obtained from MB-MWFT spectra. The main reason is that due to the low symmetry of the molecule three off-diagonal elements of the coupling tensor have to be taken into account for an exact analysis. This was not possible for reasons given above. Instead all off-diagonal elements of the coupling tensor were neglected and a first order treatment was used. Although the individual observed-minus-calculated values are rather large the high number of measured components allowed the determination of coupling constants with a reasonable accuracy. A further problem is the presence of fluorine spin-rotation coupling which caused an additional splitting of many chlorine hyperfine components. In such cases the Fourier transformation of the free induction decay was performed with only 2 or 4 K data points of a total of 8 K points. In the resulting spectra the individual lines are considerably broader and narrow multiplets become one roughly intensity weighted broad line. This also reduced the accuracy of the frequencies used in the fit.

No evidence was found for internal rotation of the trifluoromethyl group. This would have caused very narrow A-E splittings of each hfs component. No such splittings were found within the lines up to $J = 5$ which indicates that the barrier to internal rotation is rather high.

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[1] U. Andresen, H. Dreizler, J.-U. Grabow, and W. Stahl, Rev. Sci. Instrum. **61,** 3694 (1990).
[2] A complete list of measured frequencies is available under TNA23 from: Universitätsbibliothek der Universität Kiel, Olshausenstr. 40, W-2300 Kiel 1, Germany.
[3] J.-U. Grabow and W. Stahl, Z. Naturforsch. **45 a,** 1043 (1990).
[4] Program Q4 is a modified version of QUAD2 originally written by Blackman, Monash University.
[5] I. Merke, University of Kiel.
[6] Author of ZFAP4 is V. Typke, University of Ulm.