Investigation of the Microwave Spectrum of cis-Cyclopropyl Carbonyl Chloride-(^{35}Cl); Determination of the Quadrupole Coupling Tensor in its Principal Axes System

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The vibrational ground state microwave spectrum of cis-cyclopropyl carbonyl chloride-(^{35}Cl) was investigated in the region from 4 to 40 GHz by microwave Fourier transform (MWFT) spectroscopy. The rotational and fourth order centrifugal distortion constants were determined. The quadrupole hyperfine structure was assigned and the quadrupole coupling constants including the off-diagonal element χ_{ab} were evaluated. This leads to a transformation of the quadrupole coupling tensor into its principal axes system.

Introduction

The microwave spectrum of cis-cyclopropyl carbonyl chloride, C_4H_5COCl, was first observed by Nair and Boggs in 1975 [1]. Several orientations of the COCl-group with respect to the cyclopropyl frame are possible. Results of electron diffraction studies of the structure and conformational behaviour of cyclopropyl carbonyl chloride by Bartell, Guillory and Parks [2] indicated that there is a considerable surplus of the cis-isomer. They simulated radial distribution functions for various assumed concentrations of different conformers and compared them with the observed curves. Bartell et al. concluded that the equilibrium composition consists of approximately 85% ± 15% "cis-like" and 15% ± 15% "trans-like" conformers. The expression "cis-like" or "trans-like" included distorted conformations with respect to the "ideal" cis and trans isomers. This is a quite unexpected result because in general molecules predominantly favour the staggered conformation of the CH(tertiary)- and CCl-bond. In cis-cyclopropyl carbonyl chloride these bonds are eclipsed. This may result from steric effects [2].

Figure 1 shows the cis-isomer in its principal axes system of inertia in the view along the *c*-axis. The molecule possesses an *a*, *b*-plane of symmetry. The tertiary hydrogen and the chlorine atom are in cis position with respect to the C–C-bond.

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There is another interesting point about this investigation. No quadrupole coupling constants were determined so far. Moreover, a prediction of the spectrum indicates that it should be possible to evaluate the off-diagonal quadrupole coupling constant χ_{ab} directly from the spectrum. This would lead to the determination of the whole quadrupole coupling tensor in its principal axes system. Therefore, the absolute value of the angle α between the principal axes of inertia and the principal axes of the quadrupole coupling tensor should be accessible.

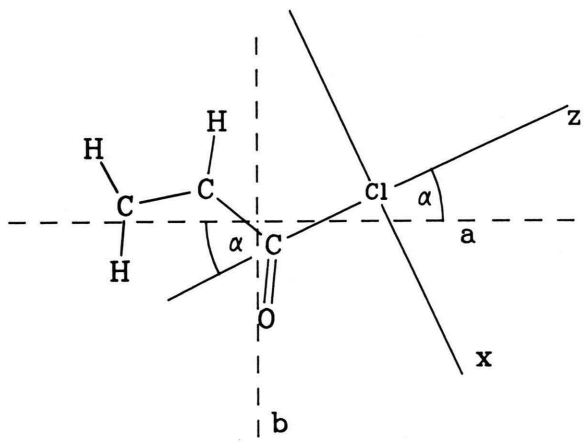

Fig. 1. Cis-cyclopropyl carbonyl chloride-(^{35}Cl) in its principal axes system of inertia (a, b, c) in the view along the *c*-axis. The *x*, *y*, *z*-axes system denotes the principal axes system of the quadrupole coupling tensor. The structure is taken from similar molecules.

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Experimental

A commercial sample of cyclopropyl carbonyl chloride (99% purity, Aldrich Chemical Co.) was used for the microwave investigation. All measurements were carried out with our standard microwave Fourier transform (MWFT) spectrometers combined with double-resonance techniques in the region from 4 to 40 GHz [3–7]. Sample pressures were about 0.2–2 mTorr (0.03–0.3 Pa) and temperatures were about −50 °C. The frequencies given here were evaluated by an iterative least squares fit of the time domain signal [8], prior to Fourier transformation.

Results and Analysis

For the first analysis we used the rotational constants of cis-cyclopropyl carbonyl chloride given in [1] and tried to assign the quadrupole hyperfine structure. The spectrum was found to be very rich with lines because of the existence of both *a*- and *b*-type-transitions, the unassigned trans (and other "trans or cis-like") conformers as well as excited vibrational states. In addition, the spectrum was complicated by the presence of the second chlorine isotopic species ^{37}Cl with the same distribution of the possible conformations.

The spectrum is highly sensitive to the polarisation conditions. Commonly, short pulses (40 to 100 ns) with extremely low input power to the travelling-wave-tube-amplifier were used [3–7]. Up to $7 \cdot 10^7$ cycles were averaged for individual transitions to yield a sufficient signal to noise ratio. The assignment was simplified and confirmed by application of double-resonance techniques with the pump/signal combinations in the V/Ku and X/K band [4]. With an iterative fit and measurement procedure, the rotational, centrifugal and quadrupole coupling constants were obtained. Subsequently, it was possible to measure transitions depending on the χ_{ab}-element. The significance of the χ_{ab}-element is emphasized in the experimental patterns of the transitions $J_{K'_-K'_+} - J_{K_-K_+} = 4_{13} - 3_{12}$ and $4_{14} - 3_{13}$, which are reproduced in Figure 2a and b. The $4_{14} - 3_{13}$ transition is nearly unperturbed, and for this reason it is symmetric with respect to a line perpendicular to the frequency axis (without consideration of the relative intensities). This symmetry is destroyed for the transition $4_{13} - 3_{12}$ by influence of the χ_{ab}-element. This off-diagonal element causes a shift of all but one hyperfine components resulting in a noticeable change of the quadrupole hyperfine structure. In particular, the $F'-F$-component 2.5–1.5 is displaced by approximately 2 MHz. Table 1 contains the energy level combinations which are strongly perturbed by the χ_{ab}-element and their corresponding

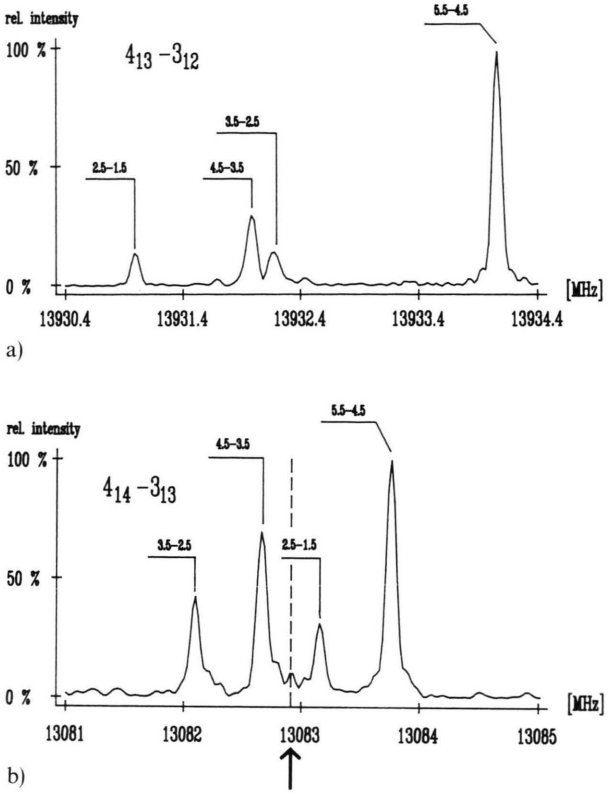

Fig. 2a and b. The transitions $(J'_{K'_-K'_+} - J_{K_-K_+}) = 4_{13} - 3_{12}$ and $4_{14} - 3_{13}$. A comparison of the two transitions shows the influence of the off-diagonal element χ_{ab} to the spectrum of cis-cyclopropyl carbonyl chloride. Each line is specified by its overall angular momentum quantum number $F'-F$. a) The perturbed transition $4_{13} - 3_{12}$: 0.5 mTorr, −50 °C, polarisation frequency: 13 993.4 MHz, sample interval: 10 ns, 1024 data points supplemented by 3072 zeros before Fourier transformation, 16 000 k experiment cycles (1 k = 1024). b) The unperturbed transition $4_{14} - 3_{13}$: 2.5 mTorr, −50 °C, polarisation frequency: 13 083 MHz, sample interval: 10 ns, 1024 data points supplemented by 3072 zeros before Fourier transformation, 28 800 k experiment cycles. ↑ indicates the position of the mirror line.

	Energy difference of the levels
$4_{13}/3_{21}$	≈22.0 MHz
$7_{25}/6_{33}$	≈60.6 MHz
$10_{38}/9_{46}$	≈32.8 MHz

Table 1. Energy level combinations which are strongly perturbed by the off-diagonal element χ_{ab}.

Table 2. Measured transition frequencies ν_{obs} and calculated frequencies ν_{calc} of cis-cyclopropyl carbonyl chloride-(^{35}Cl) with quadrupole hyperfine splitting, $\Delta\nu = \nu_{obs} - \nu_{calc}$. F is the overall angular momentum quantum number.

J'K_'K$_+$'	J K_K$_+$	F'	F	ν_{obs}/ [MHz]	ν_{calc}/ [MHz]	Δ_ν/ [kHz]
2 0 2	1 0 1	7/2	5/2	6755.089	6755.087	3
2 0 2	1 0 1	5/2	3/2	6755.138	6755.120	18
2 0 2	1 0 1	3/2	1/2	6743.423	6743.417	6
2 0 2	1 0 1	5/2	5/2	6744.304	6744.305	-1
2 0 2	1 0 1	3/2	3/2	6762.888	6762.872	16
2 0 2	1 0 1	1/2	1/2	6754.213	6754.219	-6
2 1 1	1 1 0	7/2	5/2	6976.571	6976.576	-5
2 1 1	1 1 0	5/2	3/2	6965.795	6965.796	-1
2 1 1	1 1 0	5/2	5/2	6971.294	6971.288	6
2 1 1	1 1 0	3/2	3/2	6969.572	6969.576	-4
2 1 1	1 1 0	1/2	1/2	6984.814	6984.825	-11
3 1 3	2 1 2	9/2	7/2	9819.377	9819.376	1
3 1 3	2 1 2	7/2	5/2	9816.661	9816.665	-4
3 1 3	2 1 2	5/2	3/2	9816.561	9816.560	1
3 1 3	2 1 2	3/2	1/2	9819.269	9819.257	12
3 2 1	2 1 2	9/2	7/2	25050.301	25050.284	17
3 2 1	2 1 2	7/2	5/2	25055.082	25055.097	-16
3 2 1	2 1 2	5/2	3/2	25053,373	25053.372	1
3 2 1	2 1 2	3/2	1/2	25045.370	25045.365	5
3 2 2	2 1 1	9/2	7/2	24376.051	24376.047	4
3 2 2	2 1 1	7/2	5/2	24381.337	24381.336	1
3 2 2	2 1 1	5/2	3/2	24377.561	24377.569	-8
3 2 2	2 1 1	3/2	1/2	24372.243	24372.241	2
4 1 3	3 1 2	11/2	9/2	13934.034	13934.037	-3
4 1 3	3 1 2	9/2	7/2	13931.975	13931.978	-2
4 1 3	3 1 2	7/2	5/2	13932.116	13932.115	1
4 1 3	3 1 2	5/2	3/2	13930.967	13930.974	-7
4 1 4	3 1 3	11/2	9/2	13083.735	13083.732	3
4 1 4	3 1 3	9/2	7/2	13082.637	13082.642	-4
4 1 4	3 1 3	7/2	5/2	13082.074	13082.074	0
4 1 4	3 1 3	5/2	3/2	13083.147	13083.141	5
4 2 2	3 2 1	11/2	9/2	13586.866	13586.864	2
4 2 2	3 2 1	9/2	7/2	13583.224	13583.225	-1
4 2 2	3 2 1	7/2	5/2	13582.516	13582.511	4
4 2 2	3 2 1	5/2	3/2	13589.364	13589.365	-1
4 2 3	3 2 2	11/2	9/2	13518.258	13518.264	-6
4 2 3	3 2 2	9/2	7/2	13513.975	13513.980	-4
4 2 3	3 2 2	7/2	5/2	13515.428	13515.430	-2
4 2 3	3 2 2	5/2	3/2	13519.822	13519.825	-4
4 3 1	3 3 0	11/2	9/2	13539.678	13539.678	0
4 3 1	3 3 0	9/2	7/2	13529.952	13529.947	5
4 3 1	3 3 0	7/2	5/2	13534.933	13534.932	1
4 3 1	3 3 0	5/2	3/2	13544.673	13544.660	14
4 3 2	3 3 1	11/2	9/2	13538.816	13538.814	2
4 3 2	3 3 1	9/2	7/2	13529.078	13529.084	-6
4 3 2	3 3 1	7/2	5/2	13534.068	13534.068	-0
4 3 2	3 3 1	5/2	3/2	13543.799	13543.796	3
4 1 3	4 0 4	11/2	11/2	6000.599	6000.593	6
4 1 3	4 0 4	9/2	9/2	6001.327	6001.323	4
4 1 3	4 0 4	7/2	7/2	6001.400	6001.403	-4
4 1 3	4 0 4	5/2	5/2	5997.469	5997.467	2
5 1 4	4 1 3	13/2	11/2	17402.993	17402.993	0
5 1 4	4 1 3	11/2	9/2	17403.447	17403.445	2
5 1 4	4 1 3	9/2	7/2	17402.284	17402.279	5
5 1 4	4 1 3	7/2	5/2	17405.037	17405.051	-14
5 1 5	4 0 4	13/2	11/2	20215.797	20215.791	6
5 1 5	4 0 4	11/2	9/2	20216.787	20216.793	-5
5 1 5	4 0 4	9/2	7/2	20215.757	20215.748	9
5 1 5	4 0 4	7/2	5/2	20214.833	20214.829	5
5 1 4	5 0 5	13/2	13/2	6638.280	6638.281	-2
5 1 4	5 0 5	11/2	11/2	6639.459	6639.459	0
5 1 4	5 0 5	9/2	9/2	6639.117	6639.117	0
5 1 4	5 0 5	7/2	7/2	6637.959	6637.962	-3
5 2 4	4 1 3	13/2	11/2	30390.755	30390.757	-2
5 2 4	4 1 3	11/2	9/2	30394.342	30394.340	2
5 2 4	4 1 3	9/2	7/2	30392.289	30392.291	-2
5 2 4	4 1 3	7/2	5/2	30391.909	30391.922	-12
6 3 4	6 2 5	15/2	15/2	24383.957	24383.953	3
6 3 4	6 2 5	13/2	13/2	24387.762	24387.771	-10
6 3 4	6 2 5	11/2	11/2	24386.910	24386.911	-1
6 3 4	6 2 5	9/2	9/2	24383.001	24383.006	-5
7 1 6	7 1 7	17/2	17/2	5928.042	5928.030	12
7 1 6	7 1 7	15/2	15/2	5928.252	5928.244	8
7 1 6	7 1 7	13/2	13/2	5928.190	5928.196	-5
7 1 6	7 1 7	11/2	11/2	5927.974	5927.986	-12
7 3 4	6 3 3	17/2	15/2	23732.229	23732.226	3
7 3 4	6 3 3	15/2	13/2	23729.949	23729.942	7
7 3 4	6 3 3	13/2	11/2	23730.758	23730.750	8
7 3 4	6 3 3	11/2	9/2	23731.867	23731.870	-2
8 2 6	7 2 5	19/2	17/2	27491.691	27491.696	-4
8 2 6	7 2 5	17/2	15/2	27490.589	27490.596	-6
8 2 6	7 2 5	15/2	13/2	27491.014	27491.020	-6
8 2 6	7 2 5	13/2	11/2	27490.953	27490.960	-7
8 2 7	7 2 6	19/2	17/2	26959.041	26959.045	-3
8 2 7	7 2 6	17/2	15/2	26958.583	26958.585	-2
8 2 7	7 2 6	15/2	13/2	26958.412	26958.418	-6
8 2 7	7 2 6	13/2	11/2	26958.992	26958.998	-6
8 3 5	8 2 6	19/2	19/2	23324.912	23324.905	7
8 3 5	8 2 6	17/2	17/2	23327.168	23327.169	-1
8 3 5	8 2 6	15/2	15/2	23326.778	23326.771	6
8 3 5	8 2 6	13/2	13/2	23324.487	23324.483	4
9 1 8	9 0 9	21/2	21/2	11139.007	11139.006	1
9 1 8	9 0 9	19/2	19/2	11139.454	11139.449	5
9 1 8	9 0 9	17/2	17/2	11139.374	11139.374	0
9 1 8	9 0 9	15/2	15/2	11138.934	11138.937	-3
9 2 7	9 1 8	21/2	21/2	12159.361	12159.360	1
9 2 7	9 1 8	19/2	19/2	12160.282	12160.281	1
9 2 7	9 1 8	17/2	17/2	12160.134	12160.131	3
9 2 7	9 1 8	15/2	15/2	12159.212	12159.217	-5

Table 2 (continued)

J' K'_ K'+	J K_ K+	F'	F	νobs/ [MHz]	νcalc/ [MHz]	Δν/ [kHz]	J' K_' K+'	J K_ K+	F'	F	νobs/ [MHz]	νcalc/ [MHz]	Δν/ [kHz]
9 4 6	8 4 5	21/2	19/2	30489.656	30489.654	2	10 4 6	10 3 7	23/2	23/2	33626.369	33626.367	2
9 4 6	8 4 5	19/2	17/2	30489.469	30489.468	1	10 4 6	10 3 7	21/2	21/2	33628.308	33628.320	-12
9 4 6	8 4 5	17/2	15/2	30488.612	30488.613	-1	10 4 6	10 3 7	19/2	19/2	33628.123	33628.139	-15
9 4 6	8 4 5	15/2	13/2	30491.106	30491.108	-2	10 4 6	10 3 7	17/2	17/2	33625.928	33625.922	6
10 3 7	9 3 6	23/2	21/2	34019.542	34019.539	3	10 4 7	10 3 8	23/2	23/2	33859.156	33859.150	6
10 3 7	9 3 6	21/2	19/2	34019.084	34019.082	1	10 4 7	10 3 8	21/2	21/2	33859.942	33859.931	11
10 3 7	9 3 6	19/2	17/2	34018.913	34018.918	-5	10 4 7	10 3 8	19/2	19/2	33860.888	33860.877	11
10 3 7	9 3 6	17/2	15/2	34019.668	34019.668	0	10 4 7	10 3 8	17/2	17/2	33857.804	33857.815	-11
10 3 8	9 3 7	23/2	21/2	33910.018	33910.013	5	11 5 6	10 5 5	25/2	23/2	37262.271	37262.275	-4
10 3 8	9 3 7	21/2	19/2	33910.722	33910.718	4	11 5 6	10 5 5	23/2	21/2	37261.027	37261.038	-11
10 3 8	9 3 7	19/2	17/2	33909.431	33909.428	3	11 5 6	10 5 5	21/2	19/2	37261.159	37261.165	-5
10 3 8	9 3 7	17/2	15/2	33911.037	33911.033	3	11 5 6	10 5 5	19/2	17/2	37262.375	37262.385	-10
10 4 6	9 4 5	23/2	21/2	33896.636	33896.637	-1	11 5 7	10 5 6	25/2	23/2	37262.094	37262.086	8
10 4 6	9 4 5	21/2	19/2	33895.469	33895.470	-1	11 5 7	10 5 6	23/2	21/2	37260.857	37260.849	7
10 4 6	9 4 5	19/2	17/2	33895.676	33895.679	-3	11 5 7	10 5 6	21/2	19/2	37260.983	37260.976	7
10 4 6	9 4 5	17/2	15/2	33896.580	33896.588	-8	11 5 7	10 5 6	19/2	17/2	37262.203	37262.196	7
10 4 7	9 4 6	23/2	21/2	33893.620	33893.620	0	11 6 5	10 6 4	25/2	23/2	37241.454	37241.453	1
10 4 7	9 4 6	21/2	19/2	33891.330	33891.329	1	11 6 5	10 6 4	23/2	21/2	37239.683	37239.682	1
10 4 7	9 4 6	19/2	17/2	33892.402	33892.397	5	11 6 5	10 6 4	21/2	19/2	37239.917	37239.913	4
10 4 7	9 4 6	17/2	15/2	33892.420	33892.415	5	11 6 5	10 6 4	19/2	17/2	37241.682	37241.681	1
10 7 3	9 7 2	23/2	21/2	33840.098	33840.094	4	11 7 4	10 7 3	25/2	23/2	37229.068	37229.059	9
10 7 3	9 7 2	21/2	19/2	33836.894	33836.882	12	11 7 4	10 7 3	23/2	21/2	37226.657	37226.649	8
10 7 3	9 7 2	19/2	17/2	33837.445	33837.452	-7	11 7 4	10 7 3	21/2	19/2	37227.014	37227.013	1
10 7 3	9 7 2	17/2	15/2	33840.658	33840.662	-4	11 7 4	10 7 3	19/2	17/2	37229.425	37229.420	5
10 8 2	9 8 1	23/2	21/2	33834.035	33834.048	-13							
10 8 2	9 8 1	21/2	19/2	33829.833	33829.854	-22							
10 8 2	9 8 1	19/2	17/2	33830.663	33830.650	13							
10 8 2	9 8 1	17/2	15/2	33834.836	33834.844	-7							

Shortened list of double-resonance combinations used for the confirmation of the assignment (excluded from the fit).

Singal transition				Band	Pump transition				Band
J'	K'_-	K'_+	J K_- K_+		J'	K'_-	K'_+	J K_- K_+	
4	3	1	3 3 0	Ku	3	3	0	2 2 1	V
4	1	3	3 1 2	Ku	5	2	4	4 1 3	V
5	1	5	4 0 4	K	4	0	4	3 1 3	X
3	2	2	2 1 1	K	3	1	2	2 1 1	X
3	2	1	2 1 2	K	3	2	1	2 2 0	X
7	3	4	6 3 3	K	6	4	3	7 3 4	X
8	3	5	8 2 6	K	8	2	6	8 1 7	X
6	4	3	5 4 2	K	6	4	3	7 3 4	X
7	3	4	7 2 5	K	6	4	3	7 3 4	X
6	3	4	6 2 5	K	7	1	6	6 2 5	X
9	3	6	9 2 7	K	9	2	7	9 1 8	X
7	4	4	6 4 3	K	6	4	3	7 3 4	X

energy differences. Transitions to all of these energy levels were observed. A complete list of all measured transition frequencies and a shortened schedule of double-resonance combinations used for the confirmation of the assignment are given in Table 2.

The rotational, Van Eijcks fourth order centrifugal distortion, as well as the quadrupole coupling constants including one off-diagonal element were evaluated in a one-step procedure with our program HFS.FOR. The program calculates the eigenvalues of the asymmetric top considering one coupling nucleus; it is described in detail in [9, 10]. The Hamiltonian is given in [11], the corresponding matrix elements are given in [12]. The energy matrix is set up in the coupled basis $|JKIFM_F\rangle$ in F-blocks in order of J and is then fully diagonalised. Table 3 contains the results of this analysis.

Table 3. Rotational, Van Eijck's fourth order centrifugal distortion and quadrupole coupling constants of cis-cyclopropyl carbonyl chloride-(^{35}Cl). A I^R-representation is used in the fit. The correlation matrix is given on the right side of the table. Numbers in parentheses represent single standard errors in units of last quoted digit.

		A	B	C	$\tilde{D}_J$	$\tilde{D}_{JK}$	$\tilde{D}_K$	$\tilde{\delta}_J$	$\tilde{R}_6$	χ^+	χ^-	χ_{ab}
A	6542.01009(60) MHz	1.0										
B	1796.68887(18) MHz	−0.01	1.0									
C	1583.89270(17) MHz	−0.14	−0.03	1.0								
$\tilde{D}_J$	0.23249(77) kHz	−0.13	0.54	0.63	1.0							
$\tilde{D}_{JK}$	2.1645(27) kHz	0.08	−0.03	−0.12	−0.55	1.0						
$\tilde{D}_K$	3.406(34) kHz	0.85	−0.11	−0.20	−0.07	−0.26	1.0					
$\tilde{\delta}_J$	0.02161(83) kHz	0.11	0.70	−0.67	−0.06	0.07	0.09	1.0				
$\tilde{R}_6$	0.03578(31) kHz	−0.19	0.02	0.08	0.06	0.02	−0.20	−0.10	1.0			
χ^+	43.2413(91) MHz	−0.06	−0.02	−0.0.1	−0.02	0.01	−0.05	−0.01	0.01	1.0		
χ^-	−0.837(13) MHz	−0.01	−0.06	0.02	−0.02	−0.00	−0.01	−0.05	0.00	−0.01	1.0	
$\lvert\chi_{ab}\rvert$	37.301(18) MHz	−0.09	0.29	−0.11	0.15	−0.07	−0.11	0.26	0.09	0.06	0.00	1.0

Standard deviation: 7 kHz
Fitted parameters: 11
Used number of hyperfine components for the fit: 162

Quadrupole coupling constants with respect to the principal axes system of inertia:

$\chi_{aa} = -43.2413(91)$ MHz
$\chi_{bb} = 21.202(11)$ MHz
$\chi_{cc} = 22.039(11)$ MHz
$\chi_{ab} = 37.301(18)$ MHz

$\lvert\alpha\rvert$ =	24.589(8)°
χ_{zz} =	−60.311(19) MHz
χ_{xx} =	38.271(21) MHz
χ_{yy} =	22.039(18) MHz

Table 4. Quadrupole coupling constants with respect to the principal axes system of the quadrupole coupling tensor.

The Transformation of the Quadrupole Coupling Tensor in its System of Principal Axes

The quadrupole coupling constants given in Table 3 are related to the principal axes of inertia. Because of the a, b-symmetry of cyclopropyl carbonyl chloride the tensor χ may be written in the form:

$$\chi = \begin{pmatrix} \chi_{aa} & \chi_{ab} & 0 \\ \chi_{ba} & \chi_{bb} & 0 \\ 0 & 0 & \chi_{cc} \end{pmatrix}, \quad \text{with} \quad \chi_{ab} = \chi_{ba}. \qquad (1)$$

The tensor χ may be transformed into its principal axes system by an orthogonal transformation [13]. This principle axes system is illustrated by Figure 1. α denotes the angle between the a- (system of inertia) and the z-axis (principal axes system of χ).

Table 4 contains the values of α, χ_{zz}, χ_{xx} and $\chi_{yy} = \chi_{cc}$. The errors of all constants were determined by a Gaussian error propagation (correlations between the constants are not included). As Table 4 shows they are very small. Moreover, there is no information about the sign of α. Only an isotopic substitution of the tertiary hydrogen with deuterium would lead to this information but it is difficult to prepare such a molecule. For this reason Fig. 1 is simplified because of the omission of the second (but rather less probable) orientation of the x, y, z-coordinate system.

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[1] K. P. Nair and J. E. Boggs, J. Mol. Struct. **33,** 45 (1975).
[2] L. S. Bartell, J. P. Guillory, and A. T. Parks, J. Phys. Chem. **69,** 3043 (1965).
[3] J-band: G. Bestmann, H. Dreizler, E. Fliege, and W. Stahl. J. Mol. Struct. **97,** 215 (1983).
[4] X-band: G. Bestmann and H. Dreizler, Z. Naturforsch. **37a,** 58 (1982).
[5] Ku-band: G. Bestmann, H. Dreizler, H. Mäder, and U. Andresen, Z. Naturforsch. **35a,** 392 (1980).
[6] K-band: P. Wolf and H. Mäder, J. Mol. Struct. **190,** 287 (1988).
[7] V-band: Chr. Keussen, N. Heineking, and H. Dreizler, Z. Naturforsch. **44a,** 215 (1989).
[8] J. Haekel and H. Mäder, Z. Naturforsch. **43a,** 203 (1988).
[9] J. Gripp, Dissertation, Universität Kiel 1989.
[10] J. Gripp and H. Dreizler, Z. Naturforsch. **45a,** 715 (1990).
[11] W. Gordy and R. L. Cook, Microwave Molecular Spectra, 3rd edition, John Wiley & Sons, New York 1984, Chapt. IX and XV.
[12] H. P. Benz, A. Bauder, and Hs. H. Günthard, J. Mol. Spectrosc. **21,** 156 (1966), Appendix.
[13] W. Zeil, Fortschr. Chem. Forsch. **30,** 114 (1972).