Quadrupole Hyperfine Structure in the Rotational Spectra of Sulfuryl Chloride

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The nuclear quadrupole coupling of [^{35}Cl,^{35}Cl]- and [^{35}Cl,^{37}Cl]-sulfuryl chloride, SO_2Cl_2 was investigated using waveguide microwave Fourier transform (MWFT) spectroscopy. The analysis was performed with direct diagonalization of the Hamiltonian matrix. It was possible to determine the complete coupling tensor with high accuracy. $SO_2{}^{35}Cl_2$: $\chi_{aa}(^{35}Cl1) = \chi_{aa}(^{35}Cl2) = -33.049(6)$ MHz, $\chi_{cc}(^{35}Cl1) = \chi_{cc}(^{35}Cl2) = 40.356(9)$ MHz, $\chi_{ab}(^{35}Cl1) = -\chi_{ab}(^{35}Cl2) = \pm 52.67(63)$ MHz. $SO_2{}^{35}Cl^{37}Cl$: $\chi_{aa}(^{35}Cl) = -29.582(17)$ MHz, $\chi_{cc}(^{35}Cl) = 40.340(25)$ MHz, $\chi_{ab}(^{35}Cl) = \pm 52.3(14)$ MHz, $\chi_{aa}(^{37}Cl) = -28.723(18)$ MHz, $\chi_{cc}(^{37}Cl) = 31.822(28)$ MHz, $\chi_{ab}(^{37}Cl) = \mp 37.3(19)$ MHz.

We also determined the quadrupole coupling constants in their principal axes system. In comparison with the structure, the z-axis of the coupling tensor was found to be tilted 2.0° out off the S–Cl bond axis.

Introduction

The microwave spectrum of SO_2Cl_2 was measured for the first time by Abbar [1] in 1963. In two following papers [2, 3] he supplemented his work. In [2] he also reported on the analysis of the ^{35}Cl nuclear quadrupole coupling in $SO_2{}^{35}Cl_2$. Since the spectral resolution was 100 to 200 kHz, the coupling constants had a rather large standard error of 1 MHz. Burie et al. [4] and Debrulle et al. [5] investigated the centrifugal distortion effects of $SO_2{}^{35}Cl_2$. The assignment of the rotational spectrum of $SO_2{}^{35}Cl^{37}Cl$ was reported in [6, 7].

In this work we investigated the spectra of $SO_2{}^{35}Cl_2$ and $SO_2{}^{35}Cl^{37}Cl$ with the high resolution of microwave Fourier transform (MWFT) spectroscopy [8]. It was possible to improve the accuracy of the diagonal elements and to determine the off diagonal elements of the quadrupole coupling tensor of $SO_2{}^{35}Cl_2$. Additionally we determined the quadrupole coupling of $SO_2{}^{35}Cl^{37}Cl$ for the first time [9].

Experimental

All measurements were performed with waveguide MWFT-spectrometers [10–12] in the frequency range from 6 to 26.5 GHz, at a pressure of 0.3 Pa (2 mTorr) and temperatures around 233 K (−40 °C). In the spectrum of SO_2Cl_2 the required transitions were often superimposed by strong perturbing transitions. We assume these to be high J transitions or transitions belonging to vibrationally excited states. Also lines of SO_2 were detected. In order to measure these superimposed transitions, double resonance experiments [13] were carried out.

Some selected frequencies are presented in Tables 1 and 2. A complete list is given in [9] and deposited under TNA 29 at the library of the University, D-2300 Kiel, Westring 400. In Fig. 1 we show an example for a transition without and with the double resonance technique. To eliminate overlap effects [14] the frequencies were determined by a least squares fit of the time domain signal [15].

Analysis and Discussion

The analysis of the hyperfine structure was analyzed with the program Q2DIAG described in [16]. The Hamiltonian matrix was set up in a coupled basis. The coupling scheme $I_1 + I_2 = I$, $I + J = F$ was used. The Hamiltonian is based on considerations in [17]. We used χ_{aa}, χ_{bb}, χ_{ab} and the hypothetical unsplit frequencies as fit parameters. The rotational constants for $SO_2{}^{35}Cl_2$ were fixed at the values $A = 3485.92$ MHz, $B = 2344.31$ MHz, $C = 1930.37$ MHz given in [5]. For $SO_2{}^{35}Cl^{37}Cl$ the rotational constants $A =$

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Table 1. Selected rotational transitions of sulfuryl chloride $SO_2{}^{35}Cl_2$ in the vibrational ground state. ν: measured frequency [MHz], δ_{hfs}: observed-minus-calculated frequency of the hyperfine component [kHz], ν_0: hypothetical center frequency [MHz].

$J' K'_a K'_c - J K_a K_c$ ν_0	I'	F'	I	F	ν	δ_{hfs}
1 1 1–0 0 0	2	1	2	2	5 418.632	22.5
5416.1566(56)	2	1	0	0	5 418.591	11.8
	2	2	2	2	5 416.494	3.9
	2	3	2	2	5 416.284	4.6
	0	1	2	2	5 413.968	−14.4
	0	1	0	0	5 413.924	−28.1
2 0 2–1 1 1	2	2	2	2	7 323.928	−26.4
7313.8118(56)	2	2	2	1	7 321.839	4.0
	2	4	2	3	7 313.711	6.2
	2	3	2	2	7 313.546	6.2
	0	2	0	1	7 305.594	−17.7
	0	2	2	2	7 303.132	28.0
3 1 3–2 0 2	2	3	2	2	12 973.462	−5.5
12 970.9027(39)	2	5	2	4	12 970.943	6.8
	2	4	2	3	12 970.910	4.9
	0	3	0	2	12 968.360	−6.0
4 0 4–3 1 3	0	4	2	3	15 863.143	−3.9
15 862.5654(44)	2	6	2	5	15 862.569	2.5
	2	4	0	3	15 861.986	1.5
4 1 4–3 0 3	3	7	3	6	16 613.349	0.7
16 610.9724(26)	1	4	1	3	16 613.062	−8.3
	3	6	3	5	16 611.146	3.2
	1	5	1	4	16 610.583	4.0
	1	3	1	2	16 609.320	3.7
	3	2	3	1	16 608.935	−9.9
	3	3	3	2	16 608.421	2.2
	3	5	3	4	16 608.226	4.1
	3	4	3	3	16 607.023	0.3
4 3 2–3 2 1	3	4	3	3	23 608.039	1.2
23 607.0379(27)	3	3	3	2	23 607.852	−1.8
	3	5	3	4	23 607.597	5.9
	1	3	1	2	23 607.374	−3.7
	1	5	1	4	23 607.176	−4.4
	3	6	3	5	23 606.904	5.6
	1	4	1	3	23 606.632	−2.5
	3	7	3	6	23 606.498	0.2
4 2 3–4 1 4	3	5	3	5	6 260.548	−9.3
6248.1578(19)	3	3	3	4	6 259.186	13.6
	3	7	3	6	6 258.403	4.6
	1	3	1	3	6 255.546	−8.9
	3	4	3	4	6 255.426	−8.8
	3	6	3	6	6 253.751	0.5
	1	5	1	5	6 247.180	−5.5
	3	2	3	3	6 247.019	−10.3
	3	3	3	3	6 245.022	11.4
	3	4	3	3	6 241.276	3.0
	3	7	3	7	6 240.704	−0.2
	3	2	3	2	6 239.383	5.5
	1	4	1	4	6 237.680	1.7
	3	3	3	2	6 237.371	12.1
	3	6	3	7	6 236.048	−8.4
	3	1	3	1	6 233.517	−0.8
4 3 2–4 2 3	3	5	3	5	7 032.205	1.6
7023.1618(22)	1	3	1	3	7 028.576	10.6
	3	4	3	4	7 028.471	−5.6
	3	6	3	6	7 027.254	4.8
	1	5	1	5	7 022.462	−2.3
	3	3	3	3	7 020.874	1.2
	3	3	3	2	7 018.849	−5.1
	3	2	3	3	7 018.764	−9.1
	3	7	3	7	7 017.729	2.8
	3	2	3	2	7 016.743	−11.4
	1	4	1	4	7 015.513	1.7
	3	1	3	1	7 012.474	10.6

Table 2. Selected rotational transitions of sulfuryl chloride $SO_2{}^{35}Cl^{37}Cl$ in the vibrational ground state. List of symbols see Table 1.

$J' K'_a K'_c - J K_a K_c$ ν_0	I'	F'	I	F	ν	δ_{hfs}
1 1 1–0 0 0	3	2	3	3	5350.418	−9.5
5347.4475(80)	2	1	2	2	5350.347	−0.0
	1	1	1	1	5348.545	−6.4
	3	4	3	3	5348.138	−5.1
	2	2	2	2	5347.980	0.4
	2	3	2	2	5347.779	−1.7
	1	2	1	1	5345.799	−6.1
3 2 2–3 1 3	3	4	3	4	5386.528	9.7
5372.9398(26)	0	3	0	3	5384.545	−9.0
	1	2	1	2	5381.089	3.1
	3	5	3	5	5380.580	1.5
	3	3	3	3	5378.623	−11.7
	1	4	2	4	5373.144	−3.3
	2	5	2	5	5372.767	−1.0
	2	4	1	4	5371.057	−3.8
	3	1	3	2	5366.032	−11.9
	3	6	3	6	5365.472	2.6
	2	3	2	3	5361.852	5.3
	1	3	1	3	5360.743	16.7
	3	2	3	1	5359.446	12.6
3 3 0–3 2 1	3	4	3	4	6494.181	7.3
6486.1292(26)	0	3	0	3	6492.939	−4.4
	1	2	1	2	6490.864	−3.7
	3	5	3	5	6490.412	1.3
	3	3	3	3	6489.540	2.4
	3	5	3	4	6488.940	3.1
	3	3	3	4	6487.409	−3.7
	2	5	2	5	6486.320	0.7
	2	1	2	1	6486.071	−5.7
	2	4	1	4	6485.962	1.2
	1	4	2	4	6485.341	−12.3
	3	6	3	6	6481.701	−2.1
	1	3	1	3	6479.459	18.6
	2	3	2	3	6479.086	7.0
3 3 1–3 2 2	3	4	3	4	6904.134	−6.9
6892.6212(27)	0	3	0	3	6902.425	12.1
	1	2	1	2	6899.476	−6.6
	3	5	3	5	6898.951	−6.8
	3	3	3	3	6897.444	−9.3
	2	5	2	5	6892.635	−1.3
	1	4	2	4	6891.225	3.0
	3	2	3	1	6887.054	12.3
	3	6	3	6	6886.304	−3.0
	2	3	2	3	6882.900	−6.5
	1	3	1	3	6882.685	0.2
	3	1	3	2	6881.262	9.4
4 2 3–4 1 4	3	5	3	5	6271.853	−0.7
6260.7617(27)	2	4	0	4	6270.145	1.6
	1	3	1	3	6267.414	5.5
	3	4	3	4	6267.240	5.3
	3	6	3	6	6265.973	−0.8
	2	3	2	3	6261.275	−8.6
	2	5	2	5	6261.177	−3.3
	2	6	2	6	6260.548	7.1
	1	5	1	5	6259.455	−3.3
	3	7	3	7	6254.095	−3.3
	0	4	2	4	6251.821	6.6
	1	4	1	4	6250.983	−5.3
4 3 2–4 2 3	3	5	3	5	7116.759	−2.1
7108.7773(26)	2	4	2	4	7115.506	−1.8
	1	3	1	3	7113.554	1.6
	3	4	3	4	7113.465	0.4
	3	6	3	6	7112.415	1.1
	2	5	2	5	7108.856	6.0
	2	6	2	6	7108.747	−3.1
	1	5	1	5	7108.090	1.8
	3	3	3	3	7106.672	0.8
	3	7	3	7	7103.975	−3.9
	0	4	0	4	7102.145	−7.0
	1	4	1	4	7101.912	−5.2

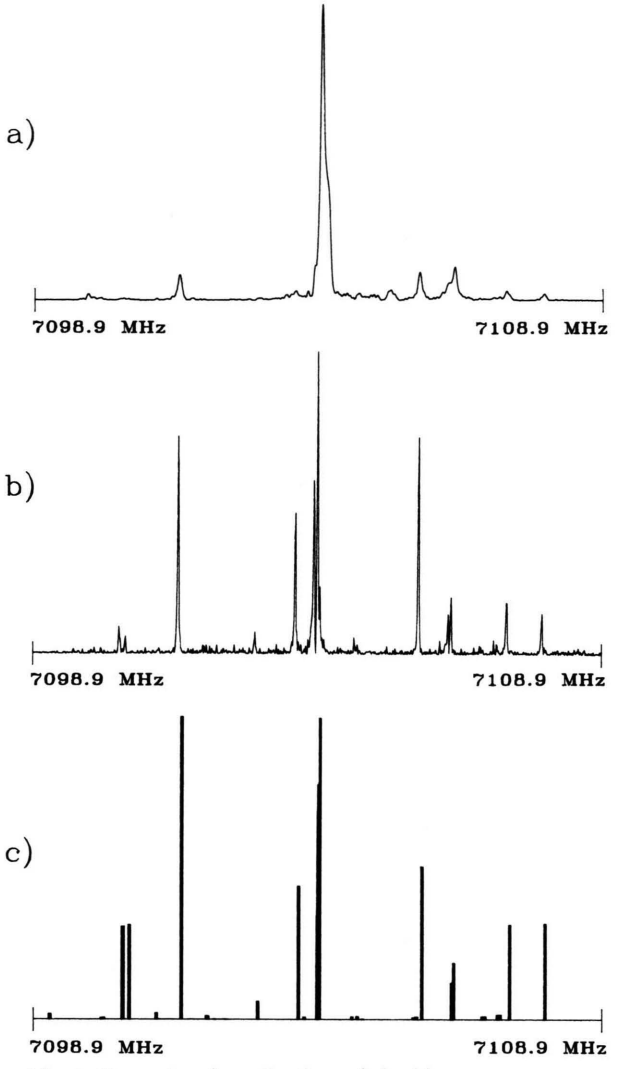

Fig. 1. Example of application of double resonance spectroscopy at the transition $J'K'_aK'_c - JK_aK_c = 4_{32}-4_{23}$ of $SO_2{}^{35}Cl^{37}Cl$. a) Without double resonance, *recording conditions:* pressure: 0.4 Pa (3.0 mTorr), polarization frequency: 7110.0 MHz, sample interval: 10 ns, averaging cycles: $3.3 \cdot 10^6$, 1024 data points supplemented with 3072 zeros prior to Fourier transformation. b) Double resonance with $5_{23}-4_{32}$ at 15 874.0 MHz. Pump power approximately 50 mW, averaging cycles: $3.3 \cdot 10^7$, all other recording conditions were equivalent to a). c) Theoretical spectrum. The correct frequency on the right hand side is 7118.9 MHz not 7108.9 MHz in a)–c).

3459.39 MHz, $B = 2293.83$ MHz, $C = 1888.16$ MHz given in [7] were used.

The axis perpendicular to the Cl–S–Cl plane is a principal axis of both the inertia and the coupling tensor (c- and y-axis, respectively). Therefore the knowledge of χ_{ab} allows the calculation of the angle

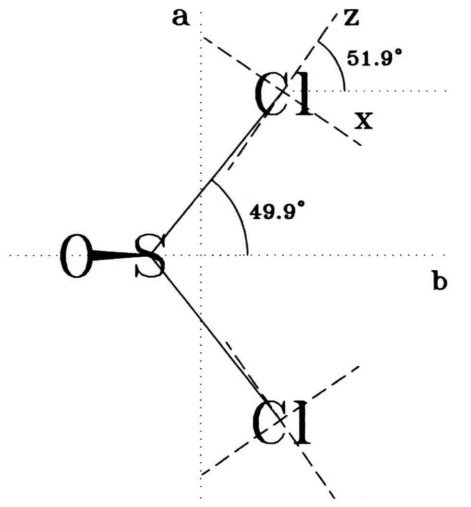

Fig. 2. Sulfuryl chloride in its principal inertia axes system (a, b). The x- and z-axes are principal axes of the quadrupole coupling tensor. The z-axis is tilted out of the S–Cl internuclear axis by 2.0°. For better recognition this angle is drawn too large in the figure.

Table 3. Quadrupole coupling constants in [MHz] of $^{35}Cl^{35}Cl$- and $^{35}Cl^{37}Cl$-sulfuryl chloride. $\chi_{gg'}$ ($g, g' = a, b, c$) coupling constants in the principal inertia axes system. $\chi_{gg'}$ ($g, g' = x, y, z$) constants in the principal axes system of the coupling tensor. θ_{za}: angle between the a-principal inertial axis and the z-principal axis of the coupling tensor in degrees. q: $\chi_{yy}(^{35}Cl)/\chi_{yy}(^{37}Cl)$. Single standard error in brackets. N: number of components included in the fit, σ: standard deviation of the fit in kHz.

$SO_2{}^{35}Cl_2$	$SO_2{}^{37}Cl^{37}Cl$
$\chi_{aa}(^{35}Cl1) = \chi_{aa}(^{35}Cl2) = -33.049(6)$	$\chi_{aa}(^{35}Cl1) = -29.582(17)$
$\chi_{bb}(^{35}Cl1) = \chi_{bb}(^{35}Cl2) = -7.307(9)$	$\chi_{bb}(^{35}Cl1) = -10.758(25)$
$\chi_{cc}(^{35}Cl1) = \chi_{cc}(^{35}Cl2) = 40.356(9)$	$\chi_{cc}(^{35}Cl1) = 40.340(25)$
$\chi_{ab}(^{35}Cl1) = -\chi_{ab}(^{35}Cl2) = \pm 52.67(63)$	$\chi_{ab}(^{35}Cl1) = \pm 52.3(14)$
	$\chi_{aa}(^{37}Cl1) = -28.723(18)$
	$\chi_{bb}(^{37}Cl1) = -3.099(28)$
	$\chi_{cc}(^{37}Cl1) = 31.822(28)$
	$\chi_{ab}(^{37}Cl1) = \mp 37.3(19)$
$\theta_{za} = \pm 38.136(79)$	$\theta_{za}(^{35}Cl) = \pm 39.90(13)$
	$\theta_{za}(^{37}Cl) = \mp 35.52(45)$
$\chi_{xx}(^{35}Cl1) = \chi_{xx}(^{35}Cl2) = 34.04(61)$	$\chi_{xx}(^{35}Cl1) = 33.0(14)$
$\chi_{yy}(^{35}Cl1) = \chi_{yy}(^{35}Cl2) = 40.3560(94)$	$\chi_{yy}(^{35}Cl1) = 40.340(25)$
$\chi_{zz}(^{35}Cl1) = \chi_{zz}(^{35}Cl2) = -74.40(61)$	$\chi_{zz}(^{35}Cl1) = -73.3(14)$
	$\chi_{xx}(^{37}Cl1) = 23.5(18)$
	$\chi_{yy}(^{37}Cl1) = 31.822(28)$
	$\chi_{zz}(^{37}Cl1) = -55.4(18)$
	$q = 1.2677(89)$
$N = 142$	$N = 126$
$\sigma = 7.7$	$\sigma = 9.1$

θ_{za} between the z-principal axis of the coupling tensor and the a-principal axis of the inertia tensor as well as the χ_{qq} ($q=x, y, z$) elements in the principal axes system of the coupling tensor. For the axes systems see Figure 2. The electronic surrounding of the chlorine nuclei in both isotopomeres can be expected to be the same. Therefore we also expect the same coupling constants χ_{qq} ($q=x, y, z$) in the principal axes system of the coupling tensor of ^{35}Cl in $SO_2{}^{35}Cl_2$ and $SO_2{}^{35}Cl^{37}Cl$. The experimental results are given in Table 3. A comparison with the structure [7] indicates that the z-axis of the coupling tensor is tilted by 2.0° with respect to the S–Cl bond axis. This supports the hypothesis of a bent bond between the sulfur and the chlorine nuclei.

Comparison of the sulfur chlorine compounds sulfur dichloride SCl_2 [18], thionyl chloride, $SOCl_2$ [19], and sulfuryl chloride, SO_2Cl_2, all of them measured with high resolution in our laboratory, is not strictly possible, as in the case of $SOCl_2$ it was not possible to determine the three off diagonal elements $\chi_{gg'}$, $g \neq g'$ of the coupling tensor. The present limitation is by computer core and time. From the results it is obvious that the substitution of two oxygen atoms at the sulfur atom changes the field gradient tensor at the chlorine atoms remarkably from $\chi_{cc}(^{35}Cl) = \chi_{yy}(^{35}Cl) = 47.7930(76)$ MHz, $\chi_{zz}(^{35}Cl) = -78.58(25)$ MHz, $\eta = (\chi_{xx}-\chi_{yy})/\chi_{zz} = 0.216(4)$ for $S^{35}Cl_2$ [18] and $\chi_{cc}(^{35}Cl) = \chi_{yy}(^{35}Cl) = 40.3560(94)$ MHz, $\chi_{zz}(^{35}Cl) = -74.40(60)$ MHz, $\eta = 0.085(9)$ for $SO_2{}^{35}Cl_2$.

For both molecules SCl_2 and SO_2Cl_2 the z axis of the coupling tensor is tilted out of the S–Cl bond axis in the same direction and order of magnitude, 1.3° in SCl_2 and 2.0° in SO_2Cl_2.

The ratio $q = Q(^{35}Cl)/Q(^{37}Cl)$ were calculated from $\chi_{yy}(^{35}Cl)/\chi_{yy}(^{37}Cl)$ avoiding an influence of the lower accuracy of χ_{ab}. We obtained $q = 1.26849(40)$ for SCl_2 and $q = 1.2677(89)$ for SO_2Cl_2. Both values agree within the error limits with $q = 1.26878(15)$ [20].

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