Nuclear Quadrupole Coupling in the Rotational Spectrum of Thionyl Chloride

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We report on the analysis of the chlorine quadrupole hyperfine structure of thionyl chloride, $SO^{35}Cl^{37}Cl$, observed with a molecular beam microwave Fourier transform spectrometer.

Introduction

Thionyl chloride, $SOCl_2$, was the object of several investigations concerning its rotational spectrum. The rotational spectrum of the main isotopomer, $SO^{35}Cl_2$, was assigned by Burie et al. [1] and Journel et al. [2, 3] yielding rotational and centrifugal distortion constants. Later Dubrulle et al. [4, 5] studied the $SO^{35}Cl^{37}Cl$ isotopomer. The ^{35}Cl quadrupole coupling constants of $SO^{35}Cl_2$ were determined by Wegner et al. [6] and confirmed by Suzuki et al. [7]. In [7] the authors also determined a r_0-structure under some assumptions and calculated the principal moments of the ^{35}Cl quadrupole coupling tensor from geometrical considerations. The $SO^{37}Cl_2$ isotopomer was assigned by Mata [8] who also improved the molecular structure.

The aim of our investigation was the precise determination of the quadrupole coupling constants of $SO^{35}Cl^{37}Cl$ and a comparison with the coupling constants of SCl_2 [9] and SO_2Cl_2 [10, 11] also determined by microwave Fourier transform (MWFT) spectroscopy [12].

Experimental

We first attempted to measure the spectra with our waveguide MWFT spectrometers [13–16], but we could not get stable measuring conditions, as presumably the substance reacted with the metal surfaces of the waveguides. Many lines of SO_2 were observed and overlayed the spectrum of $SOCl_2$. Therefore we

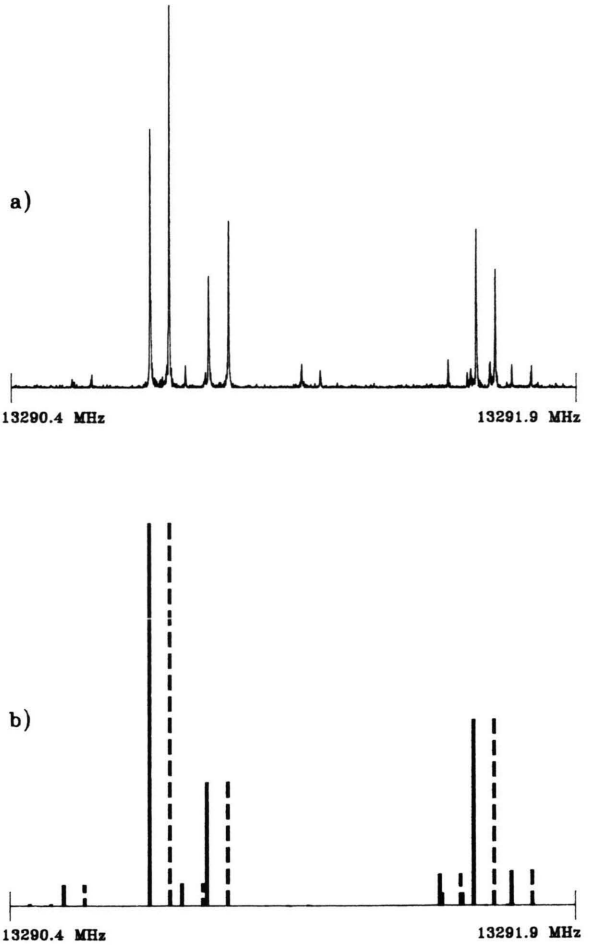

Fig. 1. A section of 1.5 MHz out of the rotational spectrum of $SO^{35}Cl^{37}Cl$ showing the transition $J_{K_aK_c} = 2_{11} - 1_{10}$. a) Polarization frequency 13 291.3 MHz, backing pressure $1 \cdot 10^6$ Pa (760 Torr), sample interval 100 ns, 2000 averaging cycles, 8192 data points supplemented by 24 578 zeros prior Fourier transition. b) Spectrum calculated with the data of Table 2. Solid and broken lines refer to lower and higher component of the Doppler doublet.

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Table 1. Rotational transitions of [^{35}Cl, ^{37}Cl]-thionyl chloride 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 0–0 0 0	1	0	1	1	7 802.399	−0.7
7793.275	2	1	0	0	7 800.549	18.2
	3	3	3	3	7 800.181	2.5
	1	2	1	1	7 797.212	−1.2
	2	3	2	2	7 793.248	−10.1
	2	2	2	2	7 793.211	−24.9
	3	4	3	3	7 791.027	26.2
	1	1	1	1	7 788.850	−1.3
	0	1	2	2	7 785.996	12.7
	3	2	3	3	7 784.950	−2.4
2 1 1–1 0 1	3	4	3	3	13 298.335	−3.1
13 291.150	3	3	3	3	13 297.841	−7.3
	2	4	3	3	13 297.464	−4.7
	1	3	1	2	13 295.285	17.1
	3	2	1	2	13 294.847	20.1
	2	3	1	2	13 294.584	10.3
	2	2	2	2	13 291.758	21.7
	3	4	2	3	13 291.663	−7.0
	1	3	2	3	13 291.649	64.1
	1	3	2	2	13 291.588	−24.4
	2	3	2	2	13 290.947	28.9
	2	3	2	3	13 290.887	−3.6
	2	4	2	3	13 290.793	−7.4
	1	2	2	2	13 290.584	23.5
	3	4	3	4	13 289.410	−21.3
	3	5	3	4	13 288.845	−5.1
	0	2	1	1	13 286.746	−22.6
	0	2	0	1	13 284.158	7.9
	3	3	3	2	13 283.070	−6.9
	1	2	3	2	13 282.427	−2.7
	2	1	3	2	13 282.385	−18.6
3 1 2–2 0 2	2	2	0	2	19 264.316	−20.2
19 257.798	3	3	3	3	19 264.153	−21.0
	3	4	3	3	19 263.097	8.0
	0	3	0	2	19 262.897	7.8
	3	5	3	4	19 262.073	7.4
	1	2	1	1	19 261.807	−3.1
	3	4	3	4	19 261.373	26.4
	3	1	3	2	19 259.654	−7.4
3 1 2–2 0 2	1	3	2	3	19 259.548	9.3
19 257.798	2	3	2	3	19 259.204	6.6
	3	2	3	2	19 258.875	−3.9
	1	4	2	3	19 258.123	−16.7
	2	5	2	4	19 257.897	2.3
	2	4	2	3	19 257.677	−8.5
	3	3	3	2	19 257.057	−0.4
	1	2	3	2	19 256.678	1.7
	1	4	1	3	19 256.356	−3.2
	0	3	2	3	19 256.212	−4.0
	2	4	1	3	19 255.898	−7.0
	3	6	3	5	19 255.256	16.0
	3	5	3	5	19 253.150	15.5
	1	3	2	2	19 252.997	0.8
	2	3	1	2	19 251.972	22.0
	3	1	3	1	19 250.938	−7.0
	2	2	1	2	19 250.403	−12.6
	3	2	3	1	19 250.140	−22.5
3 2 1–2 1 2	3	4	3	3	23 386.324	20.2
23 379.769	0	3	0	2	23 385.903	3.9
	3	5	3	4	23 384.733	−7.4
	1	2	1	1	23 384.520	0.9
	2	4	2	3	23 379.775	−3.5
	2	5	2	4	23 379.674	−34.5
	1	4	1	3	23 378.105	−24.4
	3	6	3	5	23 376.522	5.1
	2	3	2	2	23 374.006	4.1
	1	3	1	2	23 372.939	21.5
	3	1	3	1	23 371.807	24.0
3 3 0–3 2 2	3	4	3	4	13 694.993	−10.2
13 686.258	0	3	0	3	13 693.695	−3.9
	1	2	1	2	13 691.470	0.3
	3	5	3	5	13 691.077	0.5
	3	3	3	3	13 689.913	−13.2
	2	4	1	4	13 686.277	−2.1
	2	5	2	5	13 686.254	10.5
	1	4	2	4	13 685.183	13.1
	1	4	1	4	13 685.163	−3.9
	3	2	3	1	13 681.987	6.6

decided to use our molecular beam (MB) MWFT spectrometer [17, 18].

As we did not succeed to premix the $SOCl_2$ with argon, we soaked glass wool with the substance. It was positioned a few centimeters upstream the nozzle and exposed to a stream of argon at 1 bar. The content of the thionyl chloride argon mixture was unknown, but we estimate the concentration to be approximately 1% substance in argon. With the MB parallel to the resonator axis [18] we obtained a line width (HWHH) of approximately 1 kHz. The line frequencies were determined as the arithmetic mean of the Doppler doublet.

The frequencies of the measured hyperfine multiplets are given in Table 1. In Fig. 1 we show the observed and calculated pattern of the $J K_a K_c = 2_{11} - 1_{01}$ transition.

Analysis

The quadrupole hyperfine structure (hfs) of the two coupling nuclei was analyzed with the program Q2DIAG described in [19]. 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 [20].

Table 2. Quadrupole coupling constants of $SO^{35}Cl^{37}Cl$ in MHz. The quadrupole coupling constants in I were determined with a fit in which the off diagonal elements were fixed at 0 MHz. In II the results of a fit are given in which one of the off diagonal elements is fitted (see text).

	I	II
$\chi_{aa}(^{35}Cl)$	−23.008 (50)	−23.014 (39)
$\chi_{bb}(^{35}Cl)$	−2.454 (99)	−2.470 (21)
$\chi_{cc}(^{35}Cl)$	25.462 (49)	25.484 (60)
$(\chi_{ac}(^{35}Cl))$		(36.9 (12))
$\chi_{aa}(^{37}Cl)$	−21.442 (57)	−21.429 (44)
$\chi_{bb}(^{37}Cl)$	1.33 (12)	1.335 (22)
$\chi_{cc}(^{37}Cl)$	20.112 (60)	20.094 (66)
$(\chi_{ac}(^{37}Cl))$		(−35.0 (22))

As the coupling tensors in this molecule have three off diagonal elements $\chi_{gg'}$, $g, g' = a, b, c$, $g \neq g'$, a complex Hermitian matrix is to be diagonalized. Because of limited computer memory and time we restricted the analysis to a real Hermitian matrix and approximated the Hamiltonian first by neglection of all off diagonal elements and second by setting two of the three off diagonal elements equal to zero. By this second approximation the remaining off diagonal element is considered as an effective constant.

The diagonal elements χ_{gg} $g = a, b, c$ are rather insensitive to the choice of the remaining off diagonal element. Using this approximation the evaluating procedure is identical to that used for SCl_2 [9], SO_2Cl_2 [10] and $C_6H_4Cl_2$ [19].

The rotational constants were fixed at the values $A = 5044.34$ MHz, $B = 2748.94$ MHz, $C = 1918.70$ MHz given in [7]. The results are shown in Table 2. In column I all off diagonal elements are set to zero, in column II $\chi_{ac}(^{35}Cl)$ and $\chi_{ac}(^{37}Cl)$ were included in the fit. The diagonal elements are equal within the error limits.

As a determination of all off diagonal elements needs further efforts we did not determine the principal moments of the coupling tensor.

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