^{33}S Nuclear Hyperfine Structure in the Rotational Spectrum of Thiazole

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We investigated the ^{33}S nuclear quadrupole coupling of thiazole-^{33}S in natural abundance by molecular beam Fourier transform microwave spectroscopy. In addition the ^{14}N nuclear quadrupole coupling could be analyzed with high precision. We derived the rotational constants $A = 8529.29268\,(70)$ MHz, $B = 5427.47098$ MHz, and $C = 3315.21676\,(26)$ MHz, quartic centrifugal distortion constants and the quadrupole coupling constants of ^{33}S $\chi_{aa} = 7.1708\,(61)$ MHz and $\chi_{bb} = -26.1749\,(69)$ MHz and of ^{14}N $\chi_{aa} = -2.7411\,(61)$ MHz and $\chi_{bb} = 0.0767\,(69)$ MHz.

Introduction

By use of Fourier transform microwave (FTMW) spectroscopy [1, 2] it is possible to investigate the quadrupole coupling of the ^{33}S nuclei in isotopomeres of many molecules in natural abundance. This avoids difficult and expensive preparation work and extends the rare investigations on the ^{33}S hyperfine structure (hfs). A documentation about ^{33}S hfs is available from the MOGADOC data bank [3].

Further we presently investigate a series of van der Waals complexes of argon with substituted aromates and heteroaromates. One of these heteroaromates is thiazole, C_3H_3NS. We found it useful as a basis of this work to reinvestigate the rotational spectrum of the monomer, since the recent improvements of FTMW spectroscopy allow extended studies with higher sensitivity, resolution, and precision.

For thiazole the aim was the determination of the ^{33}S quadrupole coupling which can be used as a probe of the charge distribution around the ^{33}S nucleus. In course of this work, the ^{14}N quadrupole coupling, first investigated by the Copenhagen microwave laboratory [4, 5], could be analyzed more precisely. There exists a very elaborate study of the microwave spectra of thiazole and all monosubstituted isotopomers by Stark spectroscopy resulting in an r_s structure [4, 5].

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Experimental

Thiazole was purchased from Aldrich Chemie, Steinhagen, and was used without further purification. The measurements were made with our molecular beam (MB) FTMW spectrometers [6–8]. A gas mixture of 1% thiazole in argon and a stagnation pressure of 50 kPa was used throughout. The measurements of the ^{32}S, ^{34}S, and ^{33}S isotopomeres are given in the Tables 1 and 2. The Doppler splitting was eliminated by taking the mean value of the doublet components. Figure 1 gives an example for thiazole-^{33}S recorded with the spectrometer [8], which has a resonator with a quality factor $Q = 1000$ allowing to record the presented spectrum with one resonator adjustment. The line widths were 4 kHz and 10 kHz with the spectrometers [6, 7] and [8], respectively.

Spectral Analysis

The assignment of the ^{33}S isotopomer transitions was guided by taking the mean value of the frequencies of the corresponding ^{32}S and ^{34}S transitions already assigned by [5]. The rotational spectra of the thiazole-^{32}S and -^{34}S are only modified by the quadrupole coupling of the ^{14}N nucleus. The analysis uses the program HFS [9, 10] diagonalizing the Hamiltonian containing rotation, nuclear quadrupole interaction and centrifugal distortion effects accord-

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Table 1. Transition frequencies of the ^{32}S and the ^{34}S isotopomers of thiazole. ν_{obs} denotes the measured frequency, ν_{calc} the calculated frequency and $\Delta\nu = \nu_{obs} - \nu_{calc}$.

J, K_-, K_+	J', K'_-, K'_+	F	F'	Thiazole-^{32}S ν_{obs}/MHz	$\Delta\nu$/MHz	Thiazole-^{34}S ν_{obs}/MHz	$\Delta\nu$/kHz
1 0 1	0 0 0	1	1	8851.449	−1.8	8642.024	−3.3
		1	1	8849.389	−0.5	8639.974	−1.3
		2	1	8850.216	1.5	8640.796	0.1
1 1 0	1 0 1	0	1	5184.495	−1.8	5241.131	−1.8
		1	0	5184.433	0.2	5241.080	0.4
		1	1	5186.493	−0.8	5243.130	−1.4
		1	2	5185.667	−2.5	---	--
		2	1	5185.698	2.8	5242.334	2.4
		2	2	5184.872	1.2	5241.512	1.2
2 1 1	2 1 2	1	1	6483.753	−1.1	---	--
		2	1	6483.712	0.8	---	--
		3	3	6484.216	1.8	---	--
2 1 1	2 0 2	1	1	---	--	8035.928	−0.7
		3	3	---	--	8035.473	2.5
2 0 2	1 0 1	2	1	16886.637	1.2	---	--
		2	2	16885.811	−0.7	---	--
		3	2	16886.815	0.6	---	--
2 1 2	1 0 1	1	0	---	--	18390.528	0.8
		3	2	---	--	18391.282	1.6
		2	2	---	--	18390.425	−0.4
2 1 2	1 1 1	1	0	15539.378	−0.1	15216.077	−0.4
		1	1	15539.311	−3.3	---	--
		2	1	15537.981	−1.2	15214.692	0.0
		2	2	15538.009	1.2	15214.715	1.4
		3	2	15538.864	0.2	15215.570	0.5
3 0 3	2 0 2	2	2	23849.383	−1.8	---	--
		3	2	23847.799	0.1	23454.772	−0.6
		2	1	23847.828	1.8	---	--
		4	3	23847.971	0.7	23454.945	−0.3
3 3 0	3 2 1	2	2	17654.555	1.4	18418.099	−0.8
		3	3	---	--	18419.358	0.5
		4	4	17654.882	0.7	18418.427	1.1
3 1 2	3 0 3	2	2	---	--	13031.325	−0.3
		3	3	---	--	13032.499	0.1
		4	4	---	--	13031.630	−0.2
3 1 3	2 1 2	3	2	22867.146	−0.7	---	--
		2	1	22867.369	1.7	---	--
		4	3	22867.441	1.1	---	--
3 1 3	2 2 0	2	1	6500.023	2.7	---	--
		4	3	6499.059	−2.1	---	--
3 2 1	3 1 2	2	2	---	--	10195.056	−1.0
		3	3	---	--	10195.813	−1.1
		4	4	---	--	10195.252	−1.2
3 3 1	3 2 2	4	4	20962.221	1.5	---	--
		2	2	20961.803	−3.9	---	--
		3	3	20963.397	0.3	---	--
4 1 4	3 2 1	5	4	7138.975	−0.7	---	--
4 1 3	4 0 4	4	4	20531.867	1.7	---	--
		3	3	20530.839	−3.2	---	--
		5	5	20531.053	1.3	---	--
4 2 2	4 1 3	3	3	---	--	12163.523	0.0
		4	4	---	--	12164.105	0.6
		5	5	---	--	12163.642	0.6
4 3 1	4 2 2	4	4	---	--	16361.551	5.3
		5	5	---	--	16361.045	−6.3

Table 1 (continued)

J, K_-, K_+	J', K'_-, K'_+	F	F'	Thiazole-^{32}S ν_{obs}/MHz	$\Delta\nu$/MHz	Thiazole-^{34}S ν_{obs}/MHz	$\Delta\nu$/kHz
5 2 3	5 1 4	4	4	---	--	16680.813	−2.1
		5	5	---	--	16681.383	0.4
		6	6	---	--	16680.913	1.4
5 3 2	5 2 3	4	4	---	--	15184.197	−6.8
		5	5	---	--	15184.593	1.2
		6	6	---	--	15184.264	6.3
7 4 3	7 4 4	6	6	4860.482	−1.3	---	--
		7	7	4860.595	−0.1	---	--
		8	8	4860.499	1.4	---	--

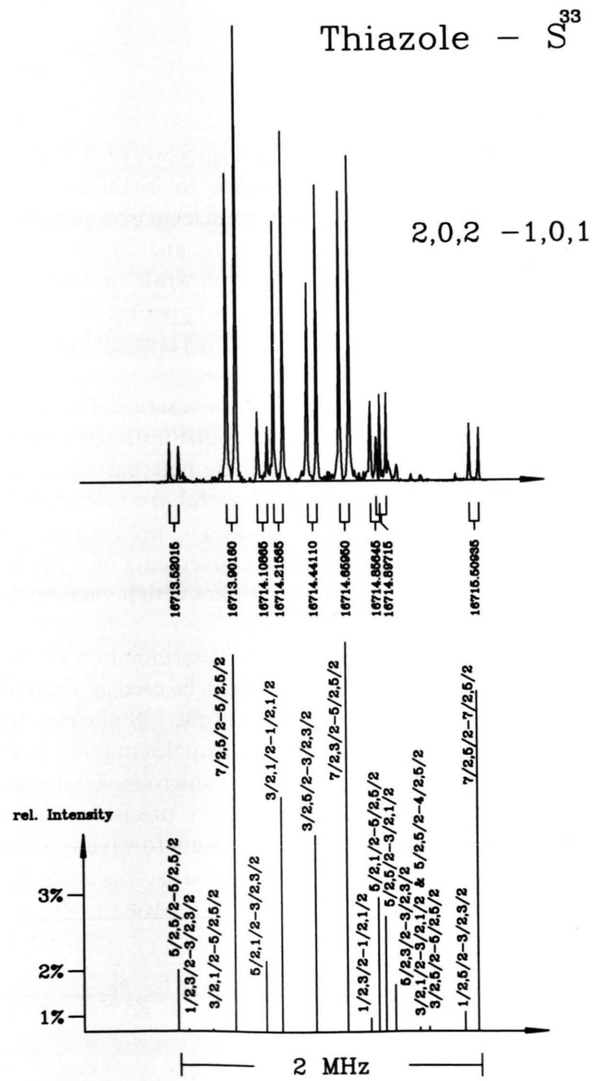

Table 2. Transition frequencies of the thiazole-^{33}S. ν_0 denotes the hyperfine free line center, ν_{obs} the measured frequency, ν_{calc} the calculated frequency and $\Delta\nu = \nu_{obs} - \nu_{calc}$. Δ_z is the error of the centrifugal distortion analysis of the hyperfine free line centers which was made by taking the arithmetic mean of the centrifugal distortion constants in the representation of van Eijck of the ^{32}S and the ^{34}S values and kept fixed in the fit. $\sigma_{hfs} = 3$ kHz denotes the standard deviation of the hyperfine structure and $\sigma_z = 1$ kHz the standard deviation of the centrifugal distortion analysis.

J, K_-, K_+ J', K'_-, K'_+ / ν_0/MHz / Δ_z/kHz	F	I	F'	I'	ν_{obs}/MHz	$\Delta\nu$/kHz
1 (1, 1) − 0 (0, 0)	1.5	2.5	0.5	0.5	11851.054	5
11844.505	1.5	0.5	0.5	0.5	11845.803	0
−1.0	3.5	2.5	2.5	2.5	11845.812	2
	2.5	1.5	1.5	1.5	11845.828	1
	1.5	1.5	0.5	0.5	11839.255	−3
	2.5	2.5	1.5	1.5	11839.272	−2
	0.5	0.5	0.5	0.5	11839.283	−3
1 (0, 1) − 0 (0, 0)	1.5	1.5	1.5	1.5	8744.821	−1
8742.684	2.5	2.5	2.5	2.5	8744.074	0
−1.0	0.5	0.5	0.5	0.5	8743.604	−1
	1.5	0.5	0.5	0.5	8742.696	1
	3.5	2.5	2.5	2.5	8742.466	4
	2.5	1.5	1.5	1.5	8741.824	2
	0.5	1.5	0.5	0.5	8740.853	−3
	1.5	2.5	1.5	1.5	8740.637	−3
1 (1, 0) − 1 (0, 1)	1.5	1.5	2.5	1.5	5218.398	−7
5214.070	2.5	2.5	3.5	2.5	5218.221	−8
1, 0	2.5	1.5	2.5	1.5	5214.380	2
	3.5	2.5	3.5	2.5	5213.211	3
	1.5	0.5	0.5	0.5	5211.874	5
	3.5	2.5	2.5	2.5	5211.603	6
	2.5	1.5	1.5	1.5	5211.383	5
	1.5	2.5	2.5	2.5	5207.784	−5
2 (1, 1) − 2 (0, 2)	2.5	0.5	2.5	1.5	8092.702	0
8095.510	4.5	2.5	4.5	2.5	8093.145	2
0.0	3.5	1.5	3.5	1.5	8093.737	−2
2 (1, 2) − 1 (1, 1)	3.5	1.5	2.5	1.5	15372.623	2
15373.106	4.5	2.5	3.5	2.5	15373.349	−1
0.0	2.5	0.5	1.5	0.5	15373.638	−2
2 (0, 2) − 1 (0, 1)	3.5	2.5	2.5	2.5	16713.904	4
16716.153	1.5	2.5	1.5	1.5	16714.443	0
1.0	3.5	1.5	2.5	2.5	16714.652	2
	2.5	0.5	2.5	2.5	16714.858	0
	2.5	2.5	1.5	0.5	16714.894	−5
	2.5	0.5	1.5	1.5	16714.106	−2
	1.5	0.5	0.5	0.5	16714.217	1
	3.5	2.5	3.5	2.5	16715.509	−1
	2.5	2.5	2.5	2.5	16713.520	0

Fig. 1. Hyperfine pattern of the $J_{K_-K_+} = 2_{02} - 1_{01}$ transition of thiazole-^{33}S measured in natural abundance (0.760%). The quantum numbers $F = I + J$ and $I = I_1 + I_2$ are given. Experimental conditions: Spectrometer [8], 8192 averaged experiment cycles, measuring time 6 min, 0.5 µs MW pulse duration, 16 k data points, 10 ns sample interval, polarizing frequency 16714.4 MHz, 1% thiazole in argon, backing pressure 50 kPa.

Table 3. Rotational constants and van Eijck's centrifugal distortion constants (I^r representation) of the sulfur isotopomers of thiazole. σ denotes the standard deviation of the lines * denotes the centrifugal constant kept fixed in the fit and $^+$ marks derived constants.

	Thiazole-^{32}S	Thiazole-^{34}S	Thiazole-^{33}S
A/MHz	8529.44879 (76)	8529.15165 (85)	8529.29268 (70)
B/MHz	5505.77663 (42)	5353.29614 (92)	5427.47098 (45)
C/MHz	3344.30259 (31)	3287.36547 (48)	3315.21676 (26)
D'_J/kHz	0.775 (13)	0.797 (38)	0.786*
D'_{JK}/kHz	0.42 (17)	0.666 (57)	0.543*
D'_K/kHz	2.02 (17)	1.82 (12)	1.97*
δ'_k/kHz	0.3343 (48)	0.322 (15)	0.328*
R'_6/kHz	−0.0630 (62)	−0.0612 (82)	−0.0621*
Quadrupole coupling constants of nitrogen:			
χ_{aa}/MHz	−2.7481 (15)	−2.7359 (23)	−2.7411 (49)
χ_{bb}/MHz	0.08505$^+$	0.0716$^+$	0.0767 (69)
χ_{cc}/MHz	2.6630$^+$	2.6664$^+$	2.6644$^+$
$\chi_{bb} - \chi_{cc}$/MHz	−2.5780 (32)	−2.5927 (47)	−2.5877$^+$
Quadrupole coupling constants of sulfur:			
χ_{aa}/MHz	---	---	7.1708 (61)
χ_{bb}/MHz	---	---	−26.1749 (69)
χ_{cc}/MHz	---	---	19.0041 (130)$^+$
$\chi_{bb} - \chi_{cc}$/MHz	---	---	−45.179$^+$
σ/kHz	1.8	2.6	3.0

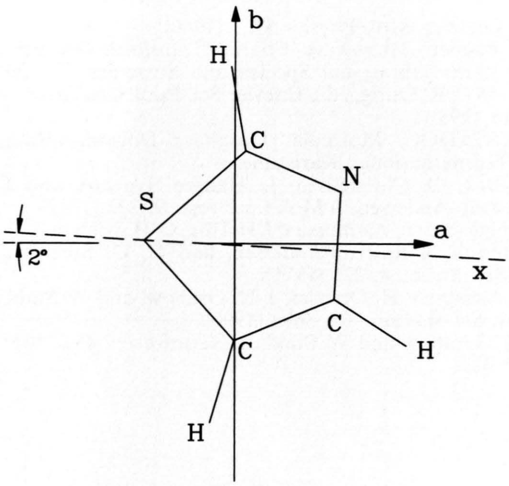

Fig. 2. Angle between the a-axis and the bisector in thiazole.

ing to van Eijck [11]. The spectrum of the ^{33}S isotopomer is modified by the two coupling nuclei ^{14}N and ^{33}S. The analysis is very complicated, as it is demonstrated in Figure 1. In this case we used the program Q4 [12, 13] based on the coupling scheme $I_1 + I_2 = I$, $I + J = F$ (I_1, I_2 nuclear spins, J angular momentum), for the analysis of the hfs splitting.

The coupling is treated as first order perturbation. The calculated hyperfine free center frequencies ν_0 provided the basis for a centrifugal distortion analysis in the formulation of van Eijck by the program ZFAP4 [14]. Since the number of measured transitions is limited, the distortion constants were fixed to the mean values of those resulting from the ^{32}S and ^{34}S spectra. The resulting rotational, centrifugal distortion and quadrupole coupling constants are given in Table 3. We could not determine off diagonal elements of the coupling tensors. Therefore the principal axes of the coupling tensors are unknown and the comparison with other ^{33}S molecules is difficult. The results should be compared with quantum chemical calculations. Assuming that one principal axis of the quadrupole coupling tensor coincides with the bisector x of the angle CSC, the principal coupling constants can be calculated [15]. The angle between the a-axis and the bisector results from the r_s structure [5] to be $\alpha = 2.0°$, as it is shown in Figure 2. The result is $\chi_{xx} = 7.21$ MHz, $\chi_{yy} = 19.0041\,(130)$ MHz and $\chi_{zz} = -26.22$ MHz. These values differ from the principal coupling constants of thiophene with $\chi_{aa} = \chi_{xx} = 6.8610\,(64)$ MHz, $\chi_{cc} = \chi_{yy} = 20.9525\,(47)$ MHz, $\chi_{bb} = \chi_{zz} = -27.8135\,(63)$ MHz [16]. It shoud be noticed that the bond angles CSC with 89.33° for thiazole [5] and 91.3° for thiophene [17] are different too.

The ^{14}N coupling constants results with higher precision. It should be mentioned that the coupling constants of the ^{33}S isotopomer agree within the error limit with the mean values of the constants of the ^{32}S and ^{34}S isotopomer.

The results for the argon-thiazole complex will be given in a forthcoming publication.

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