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

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Z. Naturforsch. **49a,** 1059–1062 (1994); received November 15, 1994

We investigated the ^{33}S nuclear quadrupole coupling in the rotational spectrum of isothiazole 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 $A = 8275.51880(80)$ MHz, $B = 5767.06181(40)$ MHz, and $C = 3396.85702(36)$ MHz, quartic centrifugal distortion constants, and the quadrupole coupling constants $\chi_{aa}(^{33}\mathrm{S}) = 8.7015(57)$ MHz, $\chi_{bb}(^{33}\mathrm{S}) = -32.9696(60)$ MHz, $\chi_{aa}(^{14}\mathrm{N}) = 1.0732(47)$ MHz and $\chi_{bb}(^{14}\mathrm{N}) = -2.4753(46)$ MHz.

Introduction

In the course of our studies on the ^{33}S nuclear quadrupole coupling we have become interested in the coupling constants of isothiazole. In previous publications we presented already some results for ^{33}S thiophene [1] and ^{33}S thiazole [2]. Using molecular beam (MB) Fourier transform microwave spectroscopy (FTMW), the high sensitivity of this method allows us to measure ^{33}S isotopomers of many molecules in natural abundance (0.75%). No difficult and expensive preparation work is needed.

First studies on isothiazole were done by Wardly et al. [3]. They derived the rotational and the ^{14}N quadrupole coupling constants of the parent molecule. Later, Wiese and Sutter [4] improved these constants considerably.

Today the best known structure of isothiazole was derived by Butterworth [5]. Using the combined techniques of double resonance and Stark modulated microwave spectroscopy he was able to investigate the 1-^{34}S, 2-^{15}N, 3-^{13}C, 4-^{13}C, 5-^{13}C, and the 5-D isotopomers. In this work we present our studies on ^{33}S-isothiazole as well as a reanalysis of the parent and ^{34}S isotopomer. We compare our results with the corresponding data of thiophene and thiazole.

Preparation of Isothiazole

Isothiazole was prepared according to a method given by Lucchesini et al. [6]. A 2.5 molar aqueous mixture of propynal and hydroxylamine-O-sulphonic acid (molar ratio 1:1) was stirred at 0 °C for 4 minutes. Propynal was obtained by oxidation of propargyl alcohol with chromium trioxide [7]. After neutralizing the mixture with sodium hydrogen carbonate, a small excess (molar ratio 1.1 : 1) of a 1.4 molar aqueous solution of sodium hydrogen sulfide was added. Then the reaction mixture was stirred for another 4 hours at room temperature and subsequently extracted with methylene chloride. The extract was dried over anhydrous sodium sulfate and, after removing the solvent, destilled over a small column.

Experimental

Using our MB-FTMW spectrometer in the range from 8 to 24 GHz [8] we measured the spectra of ^{32}S isothiazole up to $J = 6$, of the ^{34}S isotopomer up to $J = 4$, and the ^{33}S isotopomer up to $J = 3$. For highest resolution and sensitivity the beam was pulsed through one mirror propagating along the mirror axis. A gas mixture of 1% isothiazole in argon and a stagnation pressure of 50 kPa was used throughout. Frequency lists of the three sulfur isotopomers are given in Tables 1 and 2. The Doppler splitting was eliminated by taking the mean value of the doublet components. In Figure 1 a spectrum of ^{33}S isothiazole is given as an example. The Doppler splitting is

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

$J K_- K_+$	$J' K'_- K'_+$	$F F'$	^{32}S Isothiazole		^{34}S Isothiazole	
			ν_{obs}/MHz	$\Delta\nu$/kHz	ν_{obs}/MHz	$\Delta\nu$/kHz
1 0 1	0 0 0	0 1	9269.911	−2.2	9062.042	−3.3
		1 1	9270.715	1.5	9062.856	0.2
		2 1	9270.395	1.1	9062.532	1.3
1 1 1	0 0 0	0 1	11699.172	−2.5	11647.321	−0.8
		1 1	11699.916	2.4	11645.462	−1.1
		2 1	11701.023	−0.1	11646.206	2.3
2 0 2	1 0 1	1 0	17419.333	−0.2	17114.608	0.2
		2 1	17418.438	−0.0	17113.744	0.4
		3 2	17418.820	0.8	17114.102	−0.3
2 1 1	1 1 0	1 0	20962.998	0.1	20446.532	−1.5
		2 1	20963.181	−0.6	20446.724	−0.6
		3 2	20962.809	0.1	20446.348	1.0
2 1 2	1 1 1	1 0	16117.950	1.9	15802.960	0.8
		2 1	16119.098	0.2	15804.120	1.4
		2 2	16118.357	−1.3	15803.375	−0.3
		3 2	16118.808	−0.2	15803.825	0.4
2 2 0	2 1 1	1 1	8410.697	−1.9	8762.172	−1.7
		2 2	8409.561	0.9	8760.988	0.7
		3 3	8410.294	1.6	8761.750	1.2
2 1 1	2 0 2	1 1	8294.890	−2.1	8236.572	−2.2
		2 2	8396.220	0.6	8237.867	0.8
		3 3	8395.367	0.5	8237.038	2.3
2 1 2	1 0 1	1 0	–	–	18388.236	0.5
		2 1	18547.557	−1.4	18386.726	0.0
		2 2	–	–	18387.049	−1.0
		3 2	18548.328	0.3	–	–
3 0 3	2 0 2	2 1	24339.820	−1.9	23986.803	−0.8
		3 2	24339.417	0.4	23986.391	−0.1
		4 3	24339.728	2.4	23986.702	−0.3
3 0 3	2 1 2	2 1	23210.097	0.3	22713.177	0.7
		3 2	23210.297	1.0	22713.409	0.2
		4 3	23210.215	−2.1	22713.305	0.0
4 2 2	4 1 3	3 3	12821.154	0.4	12496.652	−1.0
		4 4	12821.797	−1.2	12497.242	0.2
		5 5	12821.287	0.2	12496.774	0.8
4 3 1	4 2 2	3 3	12849.752	−3.3	13504.542	−4.3
		4 4	12849.182	0.8	13503.916	3.0
		5 5	12849.640	2.3	13504.418	1.2
6 4 2	6 3 3	6 6	17036.482	−2.4	–	–
		7 7	17036.845	2.4	–	–
6 3 3	6 2 4	5 5	16991.880	4.4	–	–
		6 6	16992.330	−5.3	–	–
		7 7	16991.943	0.7	–	–

Table 2. Measured transitions of ^{33}S isothiazole. ν_0 denotes the hyperfine free line center, ν_{obs} the observed 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. $\sigma_{HFS} = 0.6$ kHz denotes the standard deviation of the hyperfine structure and $\sigma_Z = 2$ 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 0 1 0 0 0	2.5	2.5	1.5	1.5	9165.710	−1.0
9163.917	1.5	1.5	0.5	0.5	9165.517	−0.0
0.0	2.5	1.5	1.5	1.5	9163.646	4.0
	3.5	2.5	2.5	2.5	9163.432	5.0
	1.5	0.5	0.5	0.5	9163.348	2.0
	0.5	1.5	0.5	0.5	9161.737	−1.0
	1.5	2.5	1.5	1.5	9161.687	−5.0
1 1 1 0 0 0	1.5	2.5	0.5	0.5	11680.674	−4.0
11672.368	0.5	1.5	0.5	0.5	11680.613	−3.0
3.0	1.5	0.5	0.5	0.5	11674.344	−0.1
	3.5	2.5	2.5	2.5	11674.146	6.0
	2.5	1.5	1.5	1.5	11673.641	5.0
	1.5	1.5	0.5	0.5	11666.121	0.0
	2.5	2.5	2.5	2.5	11665.661	0.0
	0.5	0.5	1.5	1.5	11665.271	−3.0
2 1 2 1 1 1	3.5	2.5	2.5	2.5	15960.022	0.0
15957.617	1.5	1.5	0.5	0.5	15960.460	5.0
1.0	2.5	0.5	1.5	0.5	15957.605	1.0
	4.5	2.5	3.5	2.5	15957.679	0.0
	3.5	1.5	2.5	1.5	15957.801	−1.0
	2.5	1.5	1.5	1.5	15959.398	−3.0
2 0 2 1 0 1	2.5	0.5	1.5	0.5	17264.914	0.0
17263.716	4.5	2.5	3.5	2.5	17264.821	2.0
1.0	3.5	1.5	2.5	1.5	17264.565	2.0
	2.5	1.5	1.5	1.5	17260.591	−1.0
	3.5	2.5	2.5	2.5	17260.417	−1.0
	1.5	1.5	0.5	0.5	17260.256	−3.0
2 1 1 1 1 0	3.5	1.5	2.5	1.5	20697.146	0.0
20698.011	4.5	2.5	3.5	2.5	20696.762	−1.0
−3.0	2.5	0.5	1.5	0.5	20696.643	1.0
2 2 0 2 1 1	2.5	0.5	2.5	0.5	8591.581	−1.0
8589.438	4.5	2.5	4.5	2.5	8591.353	−3.0
−1.0	3.5	1.5	3.5	1.5	8590.728	4.0
2 1 1 2 0 2	3.5	1.5	3.5	1.5	8310.516	−1.0
8312.950	4.5	2.5	4.5	2.5	8309.805	2.0
−2.0	2.5	0.5	2.5	0.5	8309.551	−1.0
3 2 1 3 0 3	4.5	1.5	4.5	1.5	14294.004	−1.0
14293.038	5.5	2.5	5.5	2.5	14293.038	1.0
2.0						

60 kHz, the line width 10 kHz, so the Doppler pattern is completely resolved.

Spectral Analysis

The assignment of the ^{33}S species was easily done by taking the mean value of the corresponding ^{32}S and ^{34}S transitions already assigned in [9] and also reanalyzed in this work. The lines of the ^{33}S isotopomer are split by quadrupole coupling of the ^{14}N and the ^{33}S nuclei. The hyperfine free line centers were assumed to be within a few MHz around the mean value of the corresponding ^{32}S and ^{34}S frequencies.

For the analysis of the ^{32}S and ^{34}S spectra, which show only ^{14}N hyperfine structure (hfs), we used the

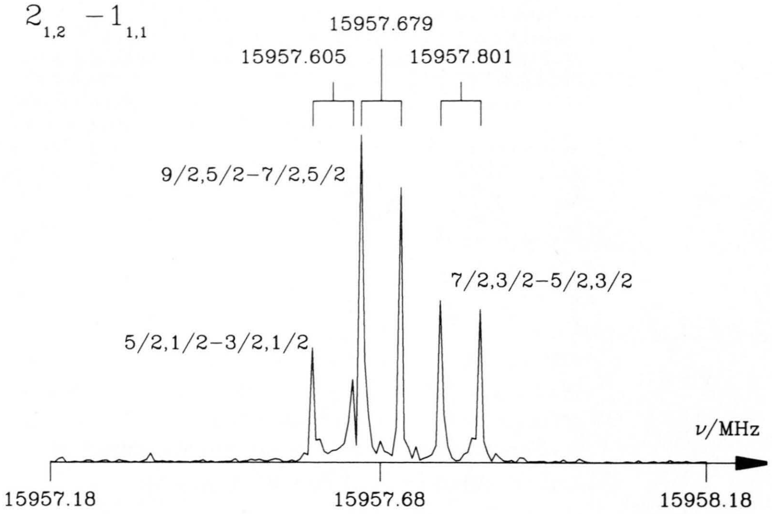

Fig. 1. Part of the hyperfine pattern of the $J_{K-,K+}=2_{1,2}-1_{1,1}$ transition of ^{33}S isothiazole measured in natural abundance (0.760%). The quantum numbers $F=J+I$ and $I=I_1+I_2$ are given. Experimental conditions: 1024 averaged experiment cycles, 0.5 μs MW pulse duration, 16 k data points, 10 ns sample intervall, polarizing frequency 15957.68 MHz, 1% isothiazole in argon, backing pressure 50 kPa.

program HFS [10, 11] which diagonalizes the Hamiltonian containing overall rotation, nuclear quadrupole coupling, and centrifugal distortion in the reduction of van Eijck [12].

In the case of ^{33}S isothiazole we used the program Q4 [13] in order to analyze the hfs splitting. The program is based on the coupling scheme

$$I_1+I_2=I,\ \ I+J=F$$

(I_1, I_2 nuclear spins, J rotational angular momentum) and treats quadrupole coupling by first order perturbation theory [14]. The resulting hyperfine free line centers ν_0 were used for a centrifugal distortion analysis in the reduction of van Eijck by the program ZFAP4 [15]. Because only a few transitions were measured, the distortion constants had to be fixed to the mean values of those resulting from the ^{32}S and ^{34}S spectra. Off diagonal elements could not be extracted from the spectra.

The resulting rotational, centrifugal distortion, and quadrupole coupling constants are given in Table 3.

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

		^{32}S Isothiazole	^{34}S Isothiazole	^{33}S Isothiazole
A'	/MHz	8275.59723 (91)	8275.44963 (72)	8275.51880 (80)
B'	/MHz	5846.2509 (15)	5691.9497 (12)	5767.06181 (40)
C'	/MHz	3424.19843 (33)	3370.63784 (29)	3396.85702 (36)
van Eijck's centrifugal distortion constants:				
D'_J	/kHz	0.756 (66)	0.685 (58)	0.721*
D'_{JK}	/kHz	0.73 (12)	0.79 (11)	0.76*
D'_K	/kHz	1.81 (23)	1.56 (21)	1.68*
δ'_K	/kHz	0.331 (55)	0.280 (48)	0.305*
R'_6	/kHz	−0.088 (29)	−0.101 (25)	−0.095*
Quadrupole coupling constants of nitrogen:				
χ_{aa}	/MHz	1.0668 (19)	1.0807 (15)	1.0732 (47)
χ_{bb}	/MHz	−2.465$^+$	−2.478$^+$	−2.4753 (46)
χ_{cc}	/MHz	1.398$^+$	1.397$^+$	1.4021$^+$
$\chi_{bb}-\chi_{cc}$	/MHz	−3.8638 (41)	−3.874 (32)	−3.8774$^+$
Quadrupole coupling constants of sulfur:				
χ_{aa}	/MHz	–	–	8.7015 (57)
χ_{bb}	/MHz	–	–	−32.9696 (60)
χ_{cc}	/MHz	–	–	24.2681$^+$
$\chi_{bb}-\chi_{cc}$	/MHz	–	–	−57.2377$^+$
σ	/kHz	2.1	1.6	0.6

Discussion

The ^{33}S quadrupole coupling constants may be compared with those of thiazole and thiophene. One way to do this is to diagonalize the coupling tensor and to compare the principal coupling constants χ_{xx}, χ_{yy}, and χ_{zz}. In the case of thiophene such a transformation is not necessary because inertial and principal coupling axes coincide for symmetry reasons. For thiazole and isothiazole it is not possible to diagonalize the coupling tensor directly since the in plane off-diagonal elements χ_{ab} could not be determined from our experimental data. Therefore we assumed as an approximation the principal x-axis to be the bisector of

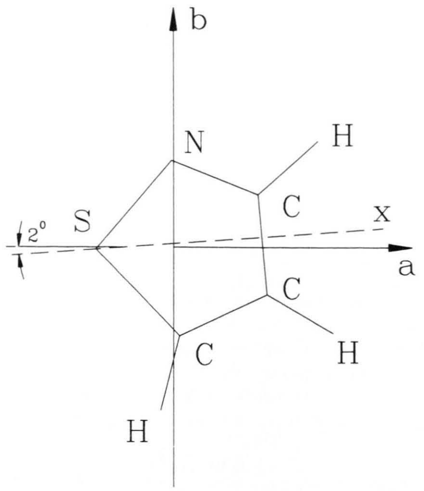

Fig. 2. Angle between the *a*-axis and the bisector *x* in isothiazole.

Table 4. Principal quadrupole coupling constants of ^{33}S. The *x*-axis is assumed to be the bisector of the CSC or CSN angle of thiazole or isothiazole, respectively. The *y*-axis is perpendicular to the ring plane.

		Thiophene	Thiazole	Isothiazole
χ_{xx}	/MHz	6.86	7.21	8.73
χ_{yy}	/MHz	20.95	19.00	24.27
χ_{zz}	/MHz	-27.81	-26.22	-33.99

the CSC or the CSN angle of thiazole or isothiazole, respectively. Rotating the tensor by the angle between inertial *a*-axis and bisector, which is 1.7° for isothiazole, approximate principal coupling elements for χ_{xx} and χ_{zz} are obtained as given in Table 4. The χ_{yy} values equal χ_{cc} since they are not influenced by a rotation around the *y*-axis being perpendicular to the ring plane. The larger coupling constants of isothiazole reflect a rather different bond situation of sulfur which is connected to C and N in isothiazole instead of two carbon atoms in thiazole and thiophene.

Acknowledgements

We thank the members of our group for help and discussion, Dr. W. Stahl for critical reading the manuscript, the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Land Schleswig-Holstein for funds.

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