The ^{33}S Nuclear Quadrupole Coupling in the Rotational Spectrum of *anti*-2,3-Dimethylthiirane

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The rotational spectrum of ^{33}S *anti*-2,3-dimethylthiirane with its ^{33}S nuclear quadrupole coupling hyperfine structure in the range 7.6 to to 21.5 GHz and its analysis is reported. The rotational constants are A = 5331.1401(5), B = 3506.3963(10), and C = 2356.9273(2) MHz. The ^{33}S quadrupole coupling constants are χ_{aa} = 8.3871(93), χ_{bb} = –32.3291(174), and χ_{cc} = 23.9420(174) MHz.

I. Introduction

The rotational spectrum of *anti*-2,3-dimethylthiirane, CH_3-C_2H_2S-CH_3, was recently investigated in our laboratory [1]. In this study the rotational spectra of the normal, ^{34}S, and ^{13}C isotopomers were measured, assigned and analysed for internal rotation and the molecular structure. The present communication aims at the nuclear quadrupole coupling of the ^{33}S isotopomer, measured in natural abundance. The nuclear quadrupole coupling tensor contains data on the S-C bonds in the thiirane ring and together with supplementary work on methylthiirane [2], CH_3-C_2H_3S, 2,2-dimethylthiirane, $(CH_3)_2$-C_2H_2S, and thiirane, C_2H_4S, we hope to get information on the effect of the methyl substitution of the thiirane ring. The results will also serve as experimental background for quantum chemical calculations [3].

This work is part in a program devoted to ^{33}S quadrupole coupling. Up to now the ^{33}S hyperfine structure of eight molecules [4 - 11] was investigated during this course by Fourier transform microwave spectroscopy [12] in our laboratory.

II. Experimental

The preparation of *anti*-2,3-dimethylthiirane is described in [1]. The spectra were recorded using a molecular beam (MB) Fourier transform microwave (FTMW) spectrometer [13] with the beam parallel to the resonator axis [14] in the region from 7.6 to 21.5 GHz. The measured low J transitions are given in Table 1. Since the transitions of the ^{32}S and ^{34}S-

Table 1. Measured transitions of ^{33}S *anti*-2,3-dimethylthiirane: $\delta\nu = \nu_{obs} - \nu_{calc}$, ν_{calc} calculated with constants of Table 2.

J'	K'_-	K'_+	J''	K''_-	K''_+	F'	F''	ν_{obs}/MHz	δ_ν/kHz
1	1	1	0	0	0	5/2	3/2	7689.67945	1.4
1	1	1	0	0	0	1/2	3/2	7696.14755	2.2
1	1	1	0	0	0	3/2	3/2	7681.5890	–7.7
2	2	1	2	1	2	7/2	7/2	8921.4520	6.5
2	2	1	2	1	2	3/2	3/2	8922.5588	3.4
2	2	1	2	1	2	3/2	5/2	8926.8280	–3.5
2	2	1	2	1	2	5/2	3/2	8921.0588	0.7
2	2	1	2	1	2	5/2	5/2	8925.3414	7.2
2	2	1	2	1	2	5/2	7/2	8919.3590	7.8
2	2	1	2	1	2	7/2	5/2	8927.4180	–10.4
2	1	2	1	0	1	7/2	5/2	12404.0300	–4.9
2	1	2	1	0	1	5/2	3/2	12395.96065	5.2
2	1	2	1	0	1	3/2	3/2	12400.23805	6.5
2	2	1	1	1	0	7/2	5/2	18352.0560	3.7
2	2	1	1	1	0	5/2	3/2	18343.96255	–10.5
2	2	1	1	1	0	3/2	1/2	18356.2318	–12.7
3	1	3	2	0	2	9/2	7/2	16722.6358	0.8
3	1	3	2	0	2	3/2	1/2	16724.75405	6.2
3	1	3	2	0	2	3/2	3/2	16725.9183	0.2
3	1	3	2	0	2	5/2	3/2	16719.6025	–3.3
3	1	3	2	0	2	5/2	5/2	16720.44695	–1.7
3	1	3	2	0	2	7/2	5/2	16717.50325	–0.6
3	1	3	2	0	2	7/2	7/2	16716.3252	–1.0
3	0	3	2	1	2	9/2	7/2	15167.42625	0.9
3	0	3	2	1	2	3/2	1/2	15165.18235	1.4
3	0	3	2	1	2	3/2	3/2	15171.1708	2.3
3	0	3	2	1	2	5/2	3/2	15166.8092	–0.1
3	0	3	2	1	2	5/2	5/2	15171.08625	0.8
3	0	3	2	1	2	7/2	5/2	15169.05495	4.5
3	0	3	2	1	2	7/2	7/2	15163.0666	–0.9
4	1	4	3	0	3	11/2	9/2	21045.3029	1.5
4	1	4	3	0	3	9/2	7/2	21042.6275	–0.6
4	1	4	3	0	3	7/2	5/2	21043.05775	–1.3
4	1	4	3	0	3	5/2	3/2	21045.7335	0.8
5	3	2	5	2	3	13/2	13/2	8686.6340	5.8

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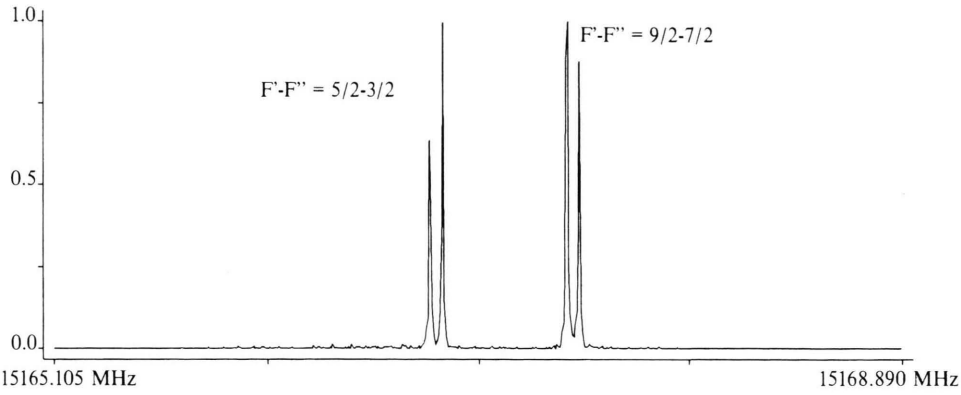

Fig. 1. Power Spectrum of two hfs components of the J', K'_-, K'_+ - J'', K''_-, K''_+ = 3, 0, 3 - 2, 1, 2 transition of ^{33}S *anti*-2,3-dimethylthiirane. Measurement conditions: 1% in argon at 50 kPa total pressure, 4 k data points at 40 ns sampling interval, 4k averaging cycles at 10 Hz repetition rate.

isotopomers were known, the ^{33}S transitions could be localized near the midfrequency of the more abundant isotopomer transitions. Here, the automatic scan mode [15] of the spectrometer was very useful. Up to 2048 measurement cycles per frequency step were used to gain a sufficient signal/noise level of the ^{33}S isotopomer in its natural abundance of 0.76%. The substance was diluted to about 1% with argon as carrier gas. A backing pressure of approximately 50 kPa was maintained for the scan and high resolution measurements. For the final high resolution measurements with 4 k data points at a sample interval of 40 ns up to 16 k experiments cycles were necessary. Figure 1 gives an example for the high resolution spectra.

III. Analysis

The measured rotational transitions splitted by nuclear quadrupole coupling were analysed with the program HFSC [16]. This program diagonalizes the hamiltonian matrix with contributions of a centrifugally distorted rotor according van Eijck [17] and quadrupole interaction [18]. No transition was sensitive to the χ_{ac} offdiagonal element of the coupling tensor. The centrifugal distortion constants were taken as fixed parameters from the ^{32}S isotopomer [1]. The resulting fitted rotational and quadrupole coupling constants are given in Table 2. We postpone the discussion of the results to a report of the results for thiirane.

A	/ MHz	=	5331.1401(5)
B	/ MHz	=	3506.3963(10)
C	/ MHz	=	2356.9273(2)
κ		=	–0.227043
D'_J	/ kHz	=	[0.5099]
D'_{JK}	/ kHz	=	[0.7231]
D'_K	/ kHz	=	[4.067]
δ'_J	/ kHz	=	[0.1896]
R'_6	/ kHz	=	[-0.0469]
χ_{aa}	/ MHz	=	8.3871(93)
$\chi_{bb}-\chi_{cc}$	/ MHz	=	–56.2711(146)
χ_{bb}	/ MHz	=	–32.3291(174)
χ_{cc}	/ MHz	=	23.9420(174)
n		=	35
σ	/ kHz	=	5.3

Table 2. Rotational, van Eijck centrifugal distortion, and quadrupole coupling constants of ^{33}S *anti*-2,3-dimethylthiirane: The centrifugal distortion constants were transferred from ^{32}S 2,3-*anti*-dimethylthiirane, n = number of components, σ = standard deviation, κ = asymmetry parameter, standard errors in brackets are in units of the last given digit, fixed values in square brackets.

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