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

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The rotational spectrum of ^{33}S 2,2-dimethylthiirane with its ^{33}S nuclear quadrupole coupling hyperfine structure in the range 8.9 to 20.0 GHz and its analysis is reported. The rotational constants are A = 5507.4663(3), B = 3440.58395(18), and C = 2978.5723(3) MHz. The ^{33}S quadrupole coupling constants are χ_{aa} = –22.6390(23), χ_{bb} = 47.1830(50), and χ_{cc} = –24.5440(50) MHz.

I. Introduction

2,2-Dimethylthiirane, $(CH_3)_2$-C_2H_2S, is the third in a series of methylsubstituted thiiranes, which we investigated for the nuclear quadrupole coupling of ^{33}S. The series will be completed by a reinvestigation of ^{33}S thiirane, C_2H_4S, itself. The results for ^{33}S methylthiirane and ^{33}S *anti*-2,3-dimethylthiirane have been reported [1, 2]. The resolution, precision and sensitivity of the molecular beam Fourier transform microwave (MB-FTMW) spectroscopy [3] allowed to reveal substitution effects.

Parallel to the study of the ^{33}S nuclear quadrupole coupling hyperfine structure, the barrier to methyl internal rotation and the structure of the heavy atom frame of these thiirane derivatives have been determined [4, 5, 6, 7]. All these efforts resulted in a broader knowledge of these substances.

II. Experimental

2,2-Dimethylthiirane was prepared according to a method proposed by Snyder, Stewart, and Ziegler [8] from 2,2-dimethyloxirane, donated by Fa. Bayer, Leverkusen. The yield was estimated to 20% - 30%. The substance was used after distillation.

The MB-FTMW spectrometer used was described elsewhere [9]. The molecular beam is arranged parallel to the resonator axis [10], thus increasing resolution and sensitivity. For the beam expansion we used 1% substance in argon at a backing pressure of approximately 50 kPa.

As the rotational spectra of the ^{32}S and ^{34}S isotopomers are known [5, 7], the transitions of the ^{33}S isotopomer in its natural abundance of 0.76% were found in the scan mode [11] of the spectrometer near the mean frequency value of the transitions of the ^{32}S and ^{34}S isotopomers. Once found, these low resolution spectra, taken with 1 k data points and up to 2 k averaging cycles, were recorded afterwards in high resolution with 4k data points and a sample interval of 40 ns using 1 k to 16 k averaging cycles, depending on the transition. Figure 1 is an example for the high resolution spectra. The observed line frequencies are given in Table 1.

III. Analysis

For the analysis we used the model of a centrifugally distorted rotor according to van Eijck/Typke [12], supplemented by nuclear quadrupole interaction [13]. The determination of the rotational, quartic centrifugal distortion, and the quadrupole coupling constants was made with the program HFSC written by Gripp [14]. The results are presented in Table 2. As only low-J lines could be measured, the centrifugal distortion constants were assumed as the mean values of those of the ^{32}S and ^{34}S isotopomers [5]. No

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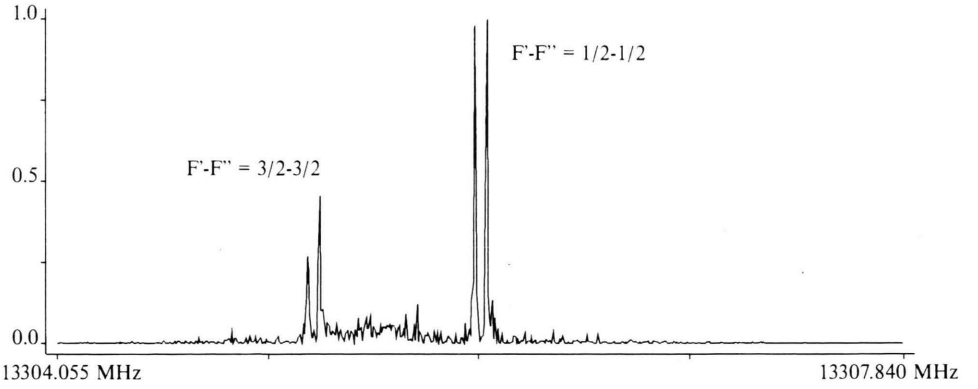

Fig. 1. Power Spectrum of two hfs components of the J', K'_-, K'_+ - J'', K''_-, K''_+ = 2, 1, 1 - 1, 1, 0 transition of ^{33}S 2,2-dimethylthiirane. Measurement conditions: 1% in argon at 50 kPa total pressure, 4 k data points at 40 ns sampling interval, 4k averaging cycles at 10 Hz repetition rate.

Table 1. Measured transitions of ^{33}S 2,2-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	0	0	0	0	1/2	3/2	8954.17805	–0.3
1	1	0	0	0	0	3/2	3/2	8943.1352	0.6
1	1	0	0	0	0	5/2	3/2	8949.2731	0.9
2	0	2	1	0	1	3/2	1/2	12763.4879	1.4
2	0	2	1	0	1	5/2	5/2	12765.2914	–1.0
2	0	2	1	0	1	1/2	1/2	12767.27605	1.9
2	0	2	1	0	1	7/2	5/2	12769.0964	–0.1
2	0	2	1	0	1	5/2	3/2	12770.95375	1.5
2	0	2	1	0	1	3/2	3/2	12773.67455	0.6
2	1	1	1	1	0	5/2	5/2	13290.64695	–1.2
2	1	1	1	1	0	3/2	1/2	13294.16215	–1.4
2	1	1	1	1	0	5/2	3/2	13296.7848	–1.0
2	1	1	1	1	0	7/2	5/2	13302.4410	–0.9
2	1	1	1	1	0	3/2	3/2	13305.2063	–1.1
2	1	1	1	1	0	1/2	1/2	13305.9632	–2.4
2	1	2	1	1	1	3/2	3/2	12366.8495	–0.5
2	1	2	1	1	1	5/2	3/2	12371.2302	0.2
2	1	2	1	1	1	7/2	5/2	12376.8866	0.1
2	1	1	1	0	1	1/2	1/2	15835.3318	1.8
2	1	1	1	0	1	3/2	1/2	15823.5293	1.3
2	1	1	1	0	1	3/2	3/2	15833.7159	0.4
2	1	1	1	0	1	5/2	3/2	15825.2974	3.5
2	1	1	1	0	1	5/2	5/2	15819.6338	–0.3
2	1	1	1	0	1	7/2	5/2	15831.4270	–0.9
2	2	0	1	1	0	3/2	3/2	19574.9889	–2.7
2	2	0	1	1	0	5/2	3/2	19577.7095	–0.5
2	2	0	1	1	0	7/2	5/2	19567.7675	2.1
2	2	1	1	1	1	3/2	3/2	19953.4976	–3.0
2	2	1	1	1	1	5/2	3/2	19957.5440	0.1
2	2	1	1	1	1	7/2	5/2	19963.6795	1.7

transition was sensitive to the off-diagonal elements of the quadrupole coupling tensor.

The discussion and interpretation of the results will be delayed until the investigation of the ^{33}S nuclear quadrupole coupling of thiirane and quantum chemical calculations on the series of methyl substituted thiiranes is completed [15].

Table 2. Rotational, van Eijck centrifugal distortion, and quadrupole coupling constants of ^{33}S 2,2-dimethylthiirane: The centrifugal distortion constants were calculated as the mean values of the ^{32}S and ^{34}S isotopomers, 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.

A	/ MHz	=	5507.46626(23)
B	/ MHz	=	3440.58395(18)
C	/ MHz	=	2978.57233(25)
κ		=	–0.6346137
D'_J	/ kHz	=	[0.6801]
D'_{JK}	/ kHz	=	[0.4697]
D'_K	/ kHz	=	[0.9157]
δ'_J	/ kHz	=	[0.09542]
R'_6	/ kHz	=	[0.01156]
χ_{aa}	/ MHz	=	–22.6390(23)
$\chi_{bb}-\chi_{cc}$	/ MHz	=	71.72701(44)
χ_{bb}	/ MHz	=	47.1830(50)
χ_{cc}	/ MHz	=	–24.5440(50)
n		=	30
σ	/ kHz	=	1.6

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