The ^{33}S Nuclear Quadrupole Coupling in the Rotational Spectrum of Methylthiirane

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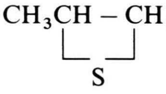
As a first example in a series of substituted thiiranes we present an investigation of the nuclear quadrupole coupling in ^{33}S-methylthiirane in natural abundance. The rotational and quadrupole coupling constants are: $A = 11\,599.0976\,(18)$ MHz, $B = 4815.6822\,(6)$MHz, $C = 3\,909.1318\,(5)$ MHz, $\chi_{aa} = -12.7731\,(82)$ MHz, $\chi_{bb} = -20.3366\,(118)$ MHz, $\chi_{cc} = 33.1097\,(273)$ MHz.

Introduction

With this publication on methylthiirane-^{33}S,  $CH_3\underset{S}{\underbrace{CH - CH_2}}$, we continue the investigation of the nuclear quadrupole coupling of ^{33}S in various molecules. As sulfur exists in very different bond situations the nuclear quadrupole coupling determined from the hyperfine structure (hfs) of rotational lines should give valuable information. These investigations became feasible by the sensitivity of molecular beam (MB) Fourier transform microwave spectrometers (FTMW) [1, 2] first described by Balle and Flygare [3], the difficult and expensive preparation of enriched isotopomers is not necessary. Up to now we investigated the ^{33}S isotopomers of the following molecules in natural abundance (0.76%):

Methylthiocyanate, $CH_3S\,CN$, [4], dimethylsulfide, $CH_3\,S\,CH_3$, [5], dimethylsulfide-d$_6$, $CD_3\,S\,CD_3$, [5], dimethylsulfoxide, $(CH_3)_2$ SO [6], dimethylsulfide, CH_3 SS CH_3, [7], isothiazole, C_3H_3 NS, [8], thiazole, $C_3\,H_3$ NS, [9], thiophene, $C_4\,H_4$ S, [10], and carbonylsulfid, OCS, [11].

With a series of substituted thiiranes we will demonstrate the influence of substitution on the quadrupole coupling tensor and the bonding. This experimental work will be supplemented by ab initio calculations.

Experimental

The substance was purchaed from Aldrich, Madrid and Steinheim, and Lancaster, Mühlheim am Main, and used without further purification. The measurements started in Valladolid, where a detailed investigation of methylthiirane (MTI) was performed with different types of spectrometers including a MB FTMW spectrometer [12] aiming the determination of the barrier to internal rotation, the dipole moment, the r_0-structure and a partial r_s-structure [13]. Later the investigation was completed using a MB FTMW spectrometer [1] in Kiel. Both MB instruments are controlled by a program written by Grabow and introduce the MB parallel to the resonator axis for higher resolution and sensitivity [2].

Gas mixtures of approximately 1% of MTI in argon or helium at a stagnation pressure around 50 kPa were used.

For the assignment of the hfs-splitted rotational lines the scan mode of the FTMW spectrometer was very useful. Up to 2 K averaging cycles for one frequency point were necessary. Regions around the mean values of low J transitions of the known ^{32}S and ^{34}S isotopomeres were covered.

The final measurements were made with 8 K points in the time domain, with 40 ns sampling interval and averaging of 1 024 to 16 384 cycles. The resulting spectral point distance is approximately 3 kHz. An example is given in Figure 1.

Table 1 shows the measured μ_a, μ_b, and μ_c lines up to $J = 3$ as the mean of the Doppler doublets. Lines with higher J values provide more difficulties for their detection, since the intensity decreases rapidly due to

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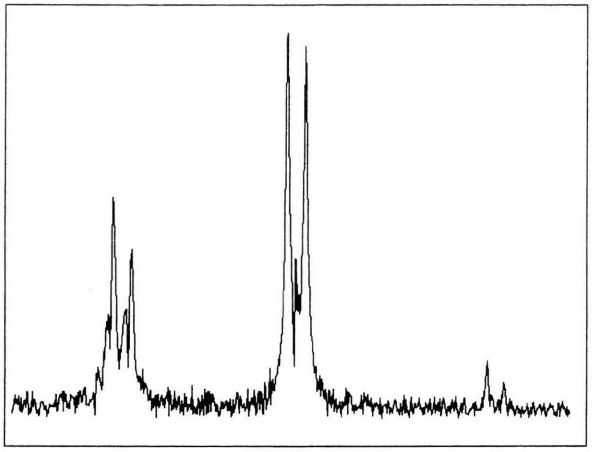

Fig. 1. A section of 1.88 MHz of the rotational amplitude spectrum of methylthiirane-^{33}S in natural abundance. In the centre, the c-type transition $J_{K-K+}=1_{10} \leftarrow 0_{00}$, $F=5/2-3/2$ appears. The weaker lines on the left and right side are unassigned. – Approximately 1% methylthiirane in argon, backing pressure 50 kPa, polarizing frequency 16413.1 MHz, 8 K points with 40 ns sample interval, 8 K averaging cycles, spectral point distance 3 kHz, S/N ≈ 23, center frequency 16413.105 MHz. Between the Doppler doublet a weak 10 MHz coherent perturbation is seen.

the depopulation of these levels during the supersonic beam expansion.

Analysis

The analysis was based on a Hamiltonian including centrifugal distortion according to Van Eijck [14] and the nuclear quadrupole coupling Hamiltonian [15]. The program HFSC of Gripp [16, 17] diagonalizes the hamiltonian matrix allowing the fit of the rotational, quartic centrifugal distortion, all quadrupole coupling, and the spin-rotation constants. The centrifugal distortion constants were fixed to the mean value of the ^{32}S and ^{34}S constants.

The parameters are given in Table 2. The fit of the absolute frequencies resulted in a standard deviation of $\sigma = 6$ kHz. The hfs splittings are in the order of some MHz.

As for this molecule, all $J = 1$-0 transitions could be measured, the coupling constants χ_{gg}, $g = a, b, c$ could be determined from three independent informations using the largest splitting of the hfs triplets [15]. The resulting values are included in Table 2, additionally to the results of the fit. It resulted that $\sum_{a,b,c} \chi_{gg} = 6$ kHz.

Table 1. List of measured rotational transitions for the ^{33}S species of methylthiirane.

J'	K'_{-1},	K'_{+1} ←	J''	K'_{-1},	K'_{+1}	F' ←	F''	ν_{observed}/MHz	$\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$/kHz
1	1	0	0	0	0	1/2	3/2	16406.493	11.3
1	1	0	0	0	0	5/2	3/2	16413.105	2.1
1	1	0	0	0	0	3/2	3/2	16421.388	7.1
1	0	1	0	0	0	1/2	3/2	8727.991	−9.0
1	0	1	0	0	0	3/2	3/2	8722.245	−7.4
1	0	1	0	0	0	5/2	3/2	8725.444	−1.5
1	1	1	0	0	0	1/2	3/2	15513.281	−13.0
1	1	1	0	0	0	3/2	3/2	15504.134	−9.1
1	1	1	0	0	0	5/2	3/2	15509.228	0.6
2	0	2	1	0	1	7/2	5/2	17365.149	−3.9
2	0	2	1	0	1	5/2	3/2	17364.339	0.5
2	0	2	1	0	1	3/2	1/2	17361.459	5.0
2	0	2	1	0	1	3/2	3/2	17367.203	2.0
2	0	2	1	0	1	1/2	1/2	17365.463	3.4
2	0	2	1	0	1	5/2	5/2	17361.141	−4.9
2	1	2	1	1	1	5/2	5/2	16536.106	−6.6
2	1	2	1	1	1	3/2	1/2	16537.966	8.7
2	1	2	1	1	1	5/2	3/2	16541.200	2.9
2	1	2	1	1	1	7/2	5/2	16544.386	−3.2
2	1	2	1	1	1	1/2	1/2	16546.241	4.7
2	1	2	1	1	1	3/2	3/2	16547.113	4.7
2	1	1	2	0	2	5/2	5/2	8687.915	0.0
2	1	1	2	0	2	7/2	7/2	8678.825	2.2
2	1	1	2	0	2	3/2	3/2	8681.419	−2.8
2	0	2	1	1	1	5/2	5/2	10577.357	−7.1
2	0	2	1	1	1	3/2	3/2	10585.316	5.4
2	0	2	1	1	1	5/2	3/2	10582.451	3.0
2	0	2	1	1	1	7/2	5/2	10581.366	−4.9
3	1	2	3	0	3	3/2	3/2	10312.904	−2.7
3	1	2	3	0	3	5/2	5/2	10322.094	−1.7
3	1	2	3	0	3	7/2	7/2	10326.388	−0.1
3	1	2	3	0	3	9/2	9/2	10317.194	2.5

Table 2. Rotational, Van Eijck centrifugal distortion and quadrupole coupling constants for the ^{33}S species of methylthiirane.

A/MHz	11599.0976	(18)[a]
B	4815.6822	(6)
C	3909.1318	(5)
D'_J/kHz	[1.839][b]	
D'_{JK}	[−2.025]	
D'_K	[16.846]	
δ_J	[0.409]	
R'_6	[−0.042]	
χ_{aa}/MHz	−12.7731	(82)
$\chi_{\min}(\chi_{bb}-\chi_{cc})$	−53.4462	(155)
χ_{bb}/MHz	−20.3366	(118)
χ_{aa}	33.1097	(273)
χ_{aa}/MHz	−12.7678	(30)[c]
χ_{bb}	−20.3269	(30)[c]
χ_{cc}	33.1018	(30)[c]
$\varkappa$[d]	−0.76423	
n[e]	32	
σ[f]/kHz	6.0	

[a] Error in brackets in units of the last digit.

[b] These values are fixed to the mean value between parent species and ^{34}S species ones.

[c] Determined from the largest splittings of the $J = 1 \leftarrow 0$ transitions. The error is derived from a measuring accuracy of 1 kHz for a component.

[d] Ray's asymmetry parameter.

[e] Number of observed components.

[f] Standard deviation of the fit.

This value should be zero as a consequence of the Laplace equation. The residuum of 6 kHz reflects the measuring accuracy which is estimated to 1 kHz. With this assumption the χ_{gg} are within the error range of the fitted values χ_{gg} using all measured lines of Table 1.

Unfortunately the experimental information is not sufficient to determine the off-diagonal nuclear quadrupole coupling tensor elements $\chi_{gg'}$, $g \neq g'$ and the spin-rotation constants [18].

The discussion and interpretation will be delayed until the investigation of the ^{33}S-hfs of thiirane, 2,2-dimethylthiirane and trans 2,3-dimethylthiirane is completed.

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[1] U. Andresen, H. Dreizler, U. Kretschmer, W. Stahl, and C. Thomsen, Fresenius J. Anal. Chem. **349,** 272 (1994).
[2] J.-U. Grabow, W. Stahl, and H. Dreizler, Rev. Sci. Instrum. in press.
[3] T. J. Balle and W. H. Flygare, Rev. Sci. Instrum. **52,** 33 (1981).
[4] N. Hansen, H. Hartwig, U. Kretschmer, and H. Mäder, Ber. Bunsenges. Phys. Chem. **100,** 1182 (1996).
[5] U. Kretschmer, H. Hartwig, and H. Dreizler, J. Mol. Spectrosc. **172,** 137 (1995).
[6] U. Kretschmer, Z. Naturforsch. **50 a,** 666 (1995).
[7] H. Hartwig, U. Kretschmer, and H. Dreizler, Z. Naturforsch. **50 a,** 131 (1995).
[8] J. Gripp, U. Kretschmer, and H. Dreizler, Z. Naturforsch. **49 a,** 1059 (1994).
[9] U. Kretschmer and H. Dreizler, Z. Naturforsch. **48 a,** 1219 (1993).
[10] U. Kretschmer, W. Stahl, and H. Dreizler, Z. Naturforsch. **448 a,** 733 (1993).
[11] I. Merke and H. Dreizler, Z. Naturforsch. **42 a,** 1043 (1987).
[12] J. L. Alonso et al., to be published.
[13] F. J. Lorenzo et al., to be published.
[14] B. P. Van Eijck, J. Mol. Spectrosc. **53,** 246 (1974).
[15] W. Gordy and R. L. Cook, Microwave Molecular Spectra, J. Wiley, New York 1984, Chapt. IX. 4.
[16] J. Gripp, Thesis in Kiel 1989.
[17] J. Gripp and H. Dreizler, Z. Naturforsch. **45 a,** 715 (1990).
[18] l.c. [15], Chapt. IX. 7.