The Rotational Spectra of the ^{32}S-, ^{33}S-, and ^{34}S-Isotopomers of Thiophene

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Z. Naturforsch. **48a**, 733–736 (1993); received April 10, 1993

The rotational spectra of the ^{32}S-, ^{34}S- and ^{33}S-isotopomers of thiophene have been studied in their natural abundances using microwave Fourier transform spectroscopy. For the ^{32}S-isotopomer the rotational and centrifugal distortion constants were found to be $A' = 8041.59407(46)$ MHz, $B' = 5418.26219(17)$ MHz, $C' = 3235.78061(16)$ MHz, $D_J' = 0.6967(96)$ kHz, $D_{JK}' = 0.530(14)$ kHz, $D_K' = 1.789(49)$ kHz, $\delta_K' = 0.3067(21)$ kHz, $R_6' = -0.0738(12)$ kHz. For the ^{34}S-isotopomer $A' = 8041.7055(84)$ MHz, $B' = 5274.1837(23)$ MHz, $C' = 3183.8432(23)$ MHz, and for the ^{33}S-isotopomer $A' = 8041.651(10)$ MHz, $B' = 5344.2988(15)$ MHz, $C' = 3209.25777(66)$ MHz with almost the same centrifugal distortion constants were obtained. The ^{33}S-quadrupole coupling constants of the ^{33}S-thiophene are $\chi_{aa} = 6.8610(64)$ MHz and $\chi_{bb} - \chi_{cc} = -48.766(11)$ MHz.

Introduction

In the course of our studies on argon van der Waals complexes we have become interested in the spectrum of the thiophene argon complex. For these investigations it turned out to be necessary to have frequency listings of all detectable isotopomers of thiophene itself. Additionally we were interested in its ^{33}S-quadrupole coupling constants.

The microwave spectra of the isotopomers of thiophene have been investigated by Bak et al. [1, 2] using a conventional Stark-modulated microwave spectrometer. They derived the r_s-structure from the rotational constants of the most abundant moiety and 2-d-, 3-d-, 3,3′-d_2-, d_4-, 2-^{13}C-, 3-^{13}C-, and ^{34}S-isotopomers. The rotational constants of the ^{34}S-isotopomer were obtained from only three transitions. Therefore we decided to use the higher resolution and sensitivity of our molecular beam (MB)- and of our waveguide (WG)-microwave Fourier transform spectrometers (MWFT) to make a complete centrifugal distortion analysis of the spectra of the three sulfur isotopomers in their natural abundances of 95.02% (^{32}S), 4.22% (^{34}S), and 0.75% (^{33}S).

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Experimental

Using our MB-MWFT spectrometer in the range from 5 to 22 GHz [3] we measured the spectra of the ^{32}S-thiophene up to $J = 7$, and of the ^{34}S- and ^{33}S-isotopomers up to $J = 4$. For highest resolution and sensitivity the beam was pulsed through one mirror propagating along the mirror axis [4]. A gas-mixture of 1% thiophene in argon and a stagnation pressure of 50 kPa was used throughout.

All higher J transitions were measured using WG-MWFT spectrometers in the range from 6 to 12 GHz [5–7]. The waveguide used as a sample cell was cooled down to 253 K and the thiophene pressure was chosen to be 2–5 mTorr (0.3–0.7 Pa).

Spectral Analysis

We started our investigation by measuring 25 transitions of the ^{32}S-isotopomer (Table 1). We determined the rotational constants and van Eijck's centrifugal distortion constants [8] in the I^r-representation by a least squares fit. In the same way we analysed 22 transitions of the ^{34}S-isotopomer (Table 2). The results of the fits are given in Table 3.

Using the structure of thiophene given in [2] we predicted the rotational constants of the ^{33}S-isotopomer. After searching for the $1_{01}-0_{00}$ and $2_{11}-1_{10}$ transitions using the automatic scan mode of the MB-MWFT spectrometer, we where able to make a better

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Table 1. Transition frequencies of the ^{32}S- and ^{34}S-isotopomers of thiophene. WG-MWFT measurements are indicated by *. ν_{obs} denotes the measured frequency, ν_{calc} the calculated frequency and $\Delta\nu = \nu_{obs} - \nu_{calc}$.

J''	K''_-	K''_+	J'	K'_-	K'_+	^{32}S-thiophene ν_{obs}/MHz	$\Delta\nu$/kHz	^{34}S-thiophene ν_{obs}/MHz	$\Delta\nu$/kHz
1	0	1	0	0	0	8 654.041	0.8	8 458.027	0.8
2	0	2	1	0	1	16 401.635	0.5	16 100.152	0.7
2	1	1	2	1	2	6 547.423	0.4	6 271.003	1.7
2	1	2	1	1	1	15 125.590	−0.6	15 825.700	−1.2
2	1	1	1	1	0	19 490.534	−0.5	19 006.363	−0.2
3	0	3	2	0	2	23 044.193	0.2	22 693.740	1.9
3	1	3	2	1	2	22 202.321	−0.2	21 798.205	−2.1
3	1	2	3	1	3	12 833.981	0.0	–	–
3	2	2	2	2	1	25 962.050	0.2	25 374.005	0.3
4	1	3	4	1	4	20 212.550	0.0	–	–
4	2	2	4	2	3	9 061.310	0.1	8 404.502	−3.3
5	3	2	5	3	3	5 111.467	−0.2	–	–
6	3	3	6	3	4	11 099.734	−0.2	–	–
7	4	3	7	4	4	6 139.040*	−1.0	5 117.039*	2.4
8	4	4	8	4	5	–	–	11 050.269*	4.5
9	5	4	9	5	5	6 958.820*	0.3	–	–
10	5	5	10	5	6	–	–	11 785.788*	−6.4
11	6	5	11	6	6	7 605.258*	−0.5	5 757.934*	−3.5
12	6	6	12	6	7	–	–	12 221.068*	−4.1
13	7	6	13	7	7	8 104.040*	0.0	5 837.586*	1.8
14	7	7	14	7	8	–	–	12 406.749*	8.2
15	8	7	15	8	8	8 475.693*	0.7	–	–
16	8	8	16	8	9	–	–	12 385.957*	0.7
17	9	8	17	9	9	8 737.352*	0.6	–	–
18	9	9	18	9	10	–	–	12 196.550*	−1.2
19	10	9	19	10	10	8 903.731*	0.5	–	–
20	10	10	20	10	11	–	–	11 872.082*	2.4
21	11	10	21	11	11	8 987.693*	−0.1	–	–
22	11	11	22	11	12	–	–	11 442.316*	1.0
23	12	11	13	12	12	9 000.604*	−0.5	–	–
24	12	12	24	12	13	–	–	10 933.505*	−7.3
25	13	12	25	23	13	8 952.582*	−0.6	–	–
27	14	13	27	14	14	8 852.656*	−0.4	–	–
28	14	14	28	14	15	–	–	9 767.141*	3.0
29	15	14	29	15	15	8 708.901*	0.7	–	–

prediction, which enabled us to find 12 different transitions with a total of 39 hyperfine components. In a global least squares fit using the program hfs [9, 10] we obtained three rotational constants, five centrifugal distortion constants and the quadrupole coupling constants χ_{aa} and $\chi_{bb} - \chi_{cc}$, also given in Table 3.

Discussion

The spectral analysis provided us with the rotational and van Eijck's centrifugal distortion constants (I^r representation) of the three sulfur isotopomers. From Table 3 it can be seen, that the constants of the ^{33}S-isotopomer are nearly the arithmetic mean of the

Table 2. Transition frequencies of the ^{33}S-isotopomer of thiophene. WG-MWFT measurements are indicated by *. ν_{obs} denotes the measured frequency, ν_{calc} the calculated frequency, ν_0 the hfs free line center and $\Delta\nu = \nu_{obs} - \nu_{calc}$.

J''	K''_-	K''_+	J'	K'_-	K'_+	ν_0	F''	F'	ν_{obs}/MHz	$\Delta\nu$/kHz
1	0	1	0	0	0	8 553.555	5/2	3/2	8 553.215	3
							1/2	3/2	8 551.836	3
							3/2	3/2	8 554.926	2
2	0	2	1	0	1	19 248.026	1/2	1/2	16 251.301	1
							5/2	3/2	16 245.537	2
							3/2	3/2	16 246.651	−2
							7/2	5/2	16 248.817	2
2	1	1	1	1	0	19 242.123	1/2	1/2	19 240.407	0
							3/2	1/2	19 247.363	1
							7/2	5/2	19 241.185	1
							3/2	3/2	19 237.929	−3
							5/2	3/2	19 242.902	2
2	1	1	2	1	2	6 405.102	7/2	7/2	6 401.618	1
							5/2	5/2	6 413.810	−1
2	1	2	1	1	1	14 972.060	5/2	5/2	14 966.924	−3
							7/2	5/2	14 972.168	1
							5/2	3/2	14 973.884	1
							3/2	1/2	14 965.106	0
							3/2	3/2	14 977.624	0
							1/2	1/2	14 970.346	1
3	0	3	2	0	2	22 865.842	9/2	7/2	22 866.858	1
							7/2	5/2	22 864.036	−1
3	1	3	2	1	2	21 995.902	9/2	7/2	21 996.289	2
							7/2	5/2	21 995.877	−3
4	2	2	4	2	3	8 721.917	11/2	11/2	8 719.164	0
7	4	3	7	4	4	5 599.521*	15/2	15/2	5 601.704	1
							13/2	13/2	5 600.948	−1
							17/2	17/2	5 597.995	3
9	5	4	9	5	5	6 198.613*	17/2	17/2	6 199.909	4
							19/2	19/2	6 200.417	2
							21/2	21/2	6 197.257	1
							15/2	15/2	6 196.755	4
10	5	5	10	5	6	12 912.051*	19/2	19/2	12 913.885	−7
							21/2	21/2	12 914.514	−8
							23/2	23/2	12 910.161	15
							17/2	17/2	12 909.515	1
11	6	5	11	6	6	6 612.490*	23/2	23/2	6 614.028	−1
							19/2	19/2	6 610.917	2
							25/2	25/2	6 611.277	0

constants of the ^{32}S- and ^{34}S-isotopomers. Using this assumption we could easily predict the transition frequencies of the ^{33}S-isotopomer.

In addition we give the freedom-cofreedom [11] and the usual correlation matrix for the rotational and centrifugal distortion constants in the lower part of Table 3. The freedom-cofreedom matrix indicates with a small diagonal element, that the associated parameter depends on the other parameters, which means no

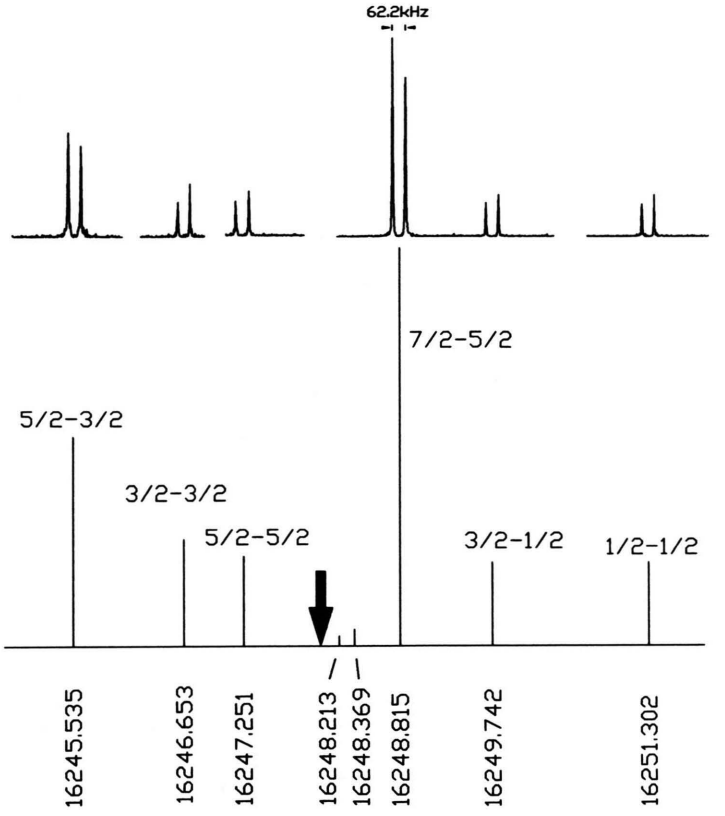

Fig. 1. Observed and calculated ^{33}S-hfs pattern of the $J_{K^-,K^+} = 2_{02} - 1_{01}$ transition of the ^{33}S-isotopomer of thiophene. The hfs components are marked by F quantum numbers of the total angular momentum. All spectra were recorded using a sample intervall of 100 ns, a microwave power of 10 mW, a microwave pulse width of 0.5 μs and a molecular pulse width of 0.25 ms to sample 8192 (8 kByte) data points. According to the intensities of the lines we used 4096–16384 averaging cycles. The intensities of the measued hyperfine components were scaled to their theoretical intensities [12]. The arrow indicates the hyperfine free line center at $\nu_0 = 16\,248.026$ MHz.

Table 3. Rotational constants and van Eijck's centrifugal distortion constants (I^r representation) of the sulfur isotopomers of thiophene. σ denotes the standard deviation of the lines. In the lower part the freedom-cofreedom and the correlation matrix is given for ^{32}S-thiophene.

	^{32}S-thiophene	^{34}S-thiophene	^{33}S-thiophene
A'/MHz	8041.59407 (46)	8041.7055 (84)	8041.651 (10)
B'/MHz	5418.26219 (17)	5274.1837 (23)	5344.2988 (15)
C'/MHz	3235.78061 (16)	3183.8432 (23)	3209.25777 (66)
D'_J/kHz	0.6967 (96)	0.64 (12)	0.604 (89)
D'_{JK}/kHz	0.530 (14)	0.68 (12)	0.88 (69)
D'_K/kHz	1.789 (49)	1.68 (54)	1.51 (86)
δ'_K/kHz	0.3067 (21)	0.287 (36)	0.297 (44)
R'_6/kHz	−0.0738 (12)	−0.082 (19)	−0.092 (38)
χ_{aa}/MHz			6.8610 (64)
$\chi_{bb}-\chi_{cc}$/MHz			−48.766 (11)
χ_{bb}/MHz			−27.8135 (63)
χ_{cc}/MHz			20.9525 (47)
σ/kHz	0.6	4.5	4.8

Correlation matrix

A'	B'	C'	D'_J	D'_{JK}	D'_K	δ'_K	R'_6
1.000							
0.691	1.000						
−0.101	0.554	1.000					
0.290	0.813	0.844	1.000				
0.185	0.045	−0.056	−0.114	1.000			
−0.132	0.050	−0.027	0.104	−0.942	1.000		
0.818	0.473	−0.420	−0.011	0.258	−0.053	1.000	
0.896	0.429	−0.386	−0.021	0.400	−0.297	0.930	1.000

Freedom-cofreedom matrix

A'	B'	C'	D'_J	D'_{JK}	D'_K	δ'_K	R'_6
0.025							
0.292	0.028						
0.459	0.365	0.048					
0.978	0.763	0.730	0.320				
0.590	0.633	0.671	0.997	0.001			
0.590	0.631	0.671	0.997	0.032	0.001		
0.440	0.581	0.628	1.000	0.138	0.132	0.001	
0.383	0.585	0.631	1.000	0.153	0.148	0.052	0.001

freedom. Small off diagonal elements indicate the path of dependence. The dependence or correlation cannot be detected easily from the correlation matrix alone.

Because of the quadrupole interaction of the ^{33}S nucleus (spin $I = 3/2$) all transitions showed a hyperfine structure (hfs). In the case of the $2_{02}-1_{01}$ transition it covers a frequency range of nearly 5.6 MHz at a hyperfine free line center of 16 248.026 MHz. Its observed and calculated hyperfine patterns are shown in Figure 1. Since only a few ^{33}S containing molecules have been studied yet, the quadrupole coupling constants of thiophene may be regarded as reference values for sulfur containing aromatic ring systems.

With our results and the data given by Bak et al. we were prepared to identify all lines due to the monomer when searching for lines of the argon van der Waals complex. The results will be published soon.

Acknowledgement

We thank the members of our group for help and discussion. Funds of the Deutsche Forschungsgemeinschaft, the Fonds der Chemie and the Land Schleswig-Holstein are gratefully acknowledged.

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