The Microwave Spectrum of the Thiophene-Argon van der Waals Complex

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The rotational spectra of the ^{32}S- and ^{34}S-thiophene-argon complex have been studied in the microwave region between 6 and 18 GHz using a pulsed molecular beam Fourier transform microwave spectrometer. The rotational and centrifugal distortion constants of the ^{32}S-thiophene-argon complex were found to be $A = 3280.38865(15)$ MHz, $B = 1203.32018(15)$ MHz, $C = 1123.45120(11)$ MHz, $\Delta_J = 3.3311(33)$ kHz, $\Delta_{JK} = 16.9015(31)$ kHz, $\Delta_K = -18.302(14)$ kHz, $\delta_J = 0.235074(86)$ kHz, $\delta_K = 4.340(33)$ kHz. For the ^{34}S-isotopomer $A = 3231.16878(15)$ MHz, $B = 1194.05602(58)$ MHz and $C = 1109.53497(30)$ MHz with almost the same centrifugal distortion constants were obtained. The argon atom is placed 3.59 Å above the ring plane.

Introduction

We extended our studies on the structure of argon van der Waals complexes with aromatic molecules [1, 2] by an investigation of the thiophene-argon complex, C_4H_4S-Ar. We analyzed the spectra of the ^{32}S- and ^{34}S-isotopomers in their natural abundance. The relatively high abundance of 4% of ^{34}S provided the possibility to observe two complex isotopomers. In future publications we will report on argon complexes with benzonitrile, 1,2,4-trifluorobenzene, 1,2,3,5-tetrafluorobenzene, oxazole and isoxazole. Further work in this field is in progress. Our study is also related to the investigation of the furane-argon complex [3–5].

Experimental

We used our molecular beam (MB) Fourier transform microwave spectrometer (FTMW) in the range from 6 to 18 GHz with its scanning mode and the molecular beam parallel to the Fabry-Perot resonator axis [6, 7]. A gas mixture of 1% thiophene (Aldrich, Steinheim) in argon and a backing pressure of 75 kPa was used throughout. For the ^{34}S-isotopomer of the complex in natural abundance up to 16 k averaging cycles were necessary to get a sufficient signal to noise ratio as displayed in Figure 1. For the normal isotopomer 1 to 8 k cycles, depending on the observed transition, were sufficient. The frequencies were determined after Fourier transformation of the 8 k time domain signal, recorded with 100 ns sample interval. This was accurate enough as only single lines appear in the spectra. A polarization power of 35 mW at a pulse length of 0.5 μs was optimal. In Table 1 we give

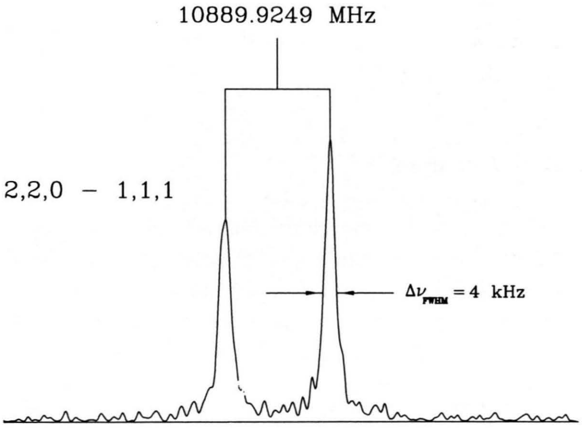

Fig. 1. The $JK_-K_+ = 2_{2,0} - 1_{1,1}$ transition of the ^{34}S-thiophene-argon complex. The doublet is due to the Doppler effect, the transition frequency is the arithmetic mean of the doublet components. The experimental accuracy is assumed to be better than 0.5 kHz. Recording conditions: Polarizing frequency at 10 889.92 MHz, MW pulse width 0.5 μs, and molecular pulse width 0.25 msec. To record the 8 k data with 100 ns sample interval and 16 384 averaged cycles we need a measuring time of approximately 11 minutes.

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Table 1. Transition frequencies of the ^{32}S- and the ^{34}S-isotopomers of the thiophene-argon van der Waals complex. ν_{obs} denotes the measured frequency, ν_{calc} the calculated frequency and $\Delta\nu = \nu_{calc} - \nu_{obs}$.

		^{32}S-thiophene-argon		^{34}S-thiophene-argon	
$J'' K''_- K''_+$	$J' K'_- K'_+$	ν_{obs}/MHz	$\Delta\nu$/kHz	ν_{obs}/MHz	$\Delta\nu$/kHz
2 1 2	1 0 1	6 650.5879	−0.2	6 559.6255	−0.3
2 2 0	1 1 1	11 046.5305	−0.2	10 889.9249	0.3
2 2 1	1 1 0	10 964.4235	0.2	10 802.8507	−0.1
2 2 1	2 1 2	6 470.7489	−0.7	–	–
2 2 0	2 1 1	6 233.4666	0.7	–	–
3 3 1	3 2 2	10 586.5791	0.5	–	–
3 3 0	3 2 1	10 575.3466	0.5	17 308.6857	−0.3
3 3 1	2 2 0	17 563.8731	0.3	17 306.0628	0.3
3 2 1	3 1 2	6 123.8557	−0.3	–	–
3 1 3	2 0 2	8 858.1220	0.2	8 737.1349	0.1
3 2 2	3 1 3	6 591.5838	1.4	6 492.8507	−0.3
4 0 4	3 1 3	7 396.6009	0.1	–	–
4 2 3	4 1 4	6 753.4636	−0.4	6 664.4007	0.2
4 1 4	3 0 3	11 029.2505	0.0	10 876.4547	0.1
4 3 2	4 2 3	10 592.0424	−0.1	10 404.9455	0.1
4 3 2	3 2 1	–	–	19 603.1099	−0.1
4 3 1	4 2 2	10 558.5930	0.0	10 366.8563	0.0
5 2 4	5 1 5	6 956.9203	−0.9	–	–
5 3 3	5 2 4	10 603.5383	−0.8	–	–
5 0 5	4 1 4	9 842.1494	0.0	–	–
5 3 2	5 2 3	10 526.3457	−0.6	–	–
6 3 3	6 2 4	10 471.9927	−0.8	–	–
6 2 5	6 1 6	7 202.4862	0.5	–	–
6 3 4	6 2 5	10 623.9602	−0.7	–	–
7 3 4	7 2 5	10 388.9089	0.8	–	–
7 3 5	7 2 6	10 656.5699	0.9	–	–

the measured frequencies as the arithmetic mean of the Doppler doublets.

Spectral Analysis

Since to our experience the intensity of ^{13}C-isotopomer transitions is similar to the intensity of complex transitions, the investigation was started by a reinvestigation of the rotational spectra of thiophene and its ^{34}S-isotopomer. In course of this work the ^{33}S-thiophene was analyzed for the first time. For this part the work of Bak et al. [8, 9] was a basis. The data for the ^{13}C-isotopomers of thiophene given in [9] were checked. The results for the ^{32}S-, ^{33}S- and ^{34}S-isotopomer, especially the ^{33}S hyperfine structure have been published [10].

After assuming a reasonable structure of the complex with the structure of thiophene being unchanged and after predicting a spectrum, we used our MB-FTMW spectrometer [6] for automatically scanning the range of 6.2 to 6.9 GHz until a preliminary assignment could be made. The final assignment of the 25 transitions up to $J = 7$ for the ^{32}S- and 12 transitions up to $J = 4$ for the ^{34}S-isotopomer was verified with a Watson's A reduction centrifugal distortion analysis [11]. The results are given in Table 2, together with the correlation and freedom-cofreedom matrices [12]. The centrifugal distortion constants for both isotopomers are rather similar and of course larger than for quasi rigid molecules.

Table 2. Rotational constants and Watson's A-centrifugal distortion constants (I^r representation) of the sulfur isotopomers of the thiophene-argon complex. σ denotes the standard deviation of the fit. In the lower part the correlation matrix and the freedom-cofreedom matrix is given for ^{32}S-thiophene-argon.

	^{32}S-thiophene-Ar	^{34}S-thiophene-Ar
A/MHz	3280.38865(15)	3231.16878(15)
B/MHz	1203.32018(15)	1194.05602(58)
C/MHz	1123.45120(11)	1109.53497(30)
Δ_J/kHz	3.3311(33)	3.265(12)
Δ_{JK}/kHz	16.9015(31)	16.239(30)
Δ_K/kHz	−18.302(14)	−17.408(19)
δ_J/kHz	0.235074(86)	0.2619(68)
δ_K/kHz	4.340(33)	4.43(14)
σ/kHz	0.72	0.36

Correlation matrix

A	B	C	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K
1.00							
0.17	1.00						
0.27	0.36	1.00					
0.20	0.86	0.66	1.00				
0.19	−0.25	0.10	−0.13	1.00			
0.67	−0.34	−0.22	−0.37	−0.20	1.00		
0.31	0.39	−0.10	0.21	0.16	0.13	1.00	
−0.25	0.36	−0.41	0.11	−0.52	−0.15	−0.30	1.00

Freedom-cofreedom matrix

A	B	C	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K
0.26							
0.97	0.23						
0.93	0.93	0.27					
0.99	0.67	0.84	0.34				
0.71	0.96	0.95	0.99	0.39			
0.49	0.93	0.96	0.96	0.68	0.24		
0.97	0.78	0.79	0.99	0.99	0.99	0.34	
0.96	0.86	0.66	0.99	0.89	0.98	0.69	0.27

Determination of the Structure

As six rotational constants were determined, for the thiophene-argon complex only limited information

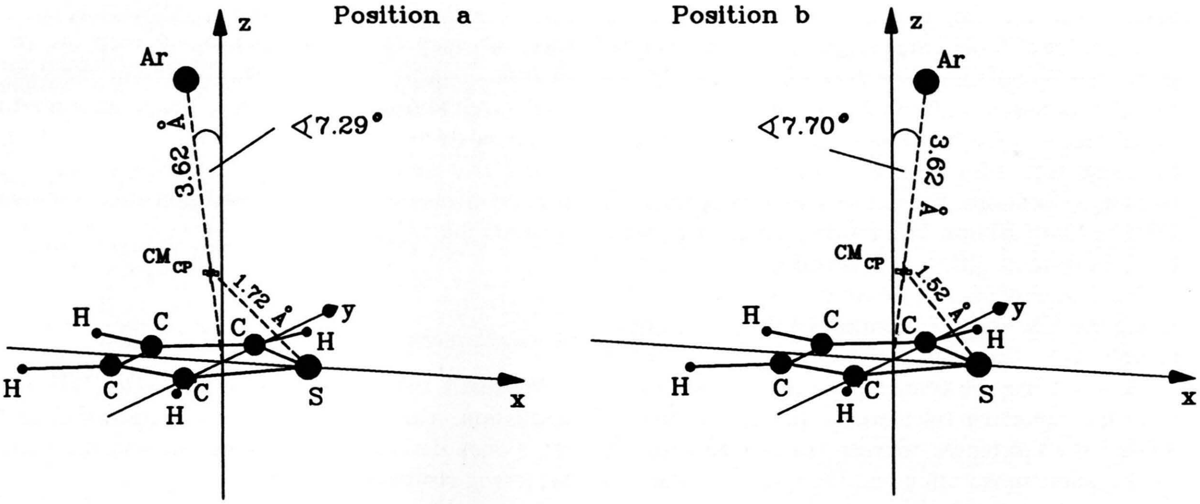

Fig. 2. The two mathematically possible structures of the thiophene-argon complex. The origin of the coordinate system is the center of mass of the thiophene molecule. The sulfur substitution in the complex let us propose that position "a" is the physically significant one.

can be obtained. As usual, the structure of the monomer is assumed to be unaffected by the complexation (Table IV of [9]).

We define a coordinate system centered at the center of mass, CM_{mol}, of the ^{32}S-thiophene. The positive x-axis is directed to the sulfur atom, the z-axis is perpendicular on the molecular plane and the y-axis completes a right handed system as given in Figure 2. In a first procedure the position of the argon atom with respect to the planar ring was derived by a r_0-like fitting procedure. The fit variables are the distance from the center of mass of thiophene CM_{mol} to the argon atom and the angle ∢ (Ar, CM_{mol}, S). C_s symmetry of the complex was assumed, so that the y-coordinate of the argon atom in our coordinate system is chosen to be $y_{Ar} = 0$. The results are given in the first two colums of Table 3. Similar to other cases [1–4], two mathematically possible positions a and b resulted for the argon atom above (and below) the ring plane. The convergence to the two positions depends on the initial conditions of the fit. The other entries of the first two columns of Table 3 are derived.

In a second r_s-like procedure [2] we calculated the position of the argon atom considering a thiophene-argon complex with an argon atom of zero mass as the mother molecule and substituting then the real argon atom mass. Here the positions x_{Ar} and z_{Ar} resulted [13]. The assumed C_s symmetry of the complex leads to $y_{Ar} = 0$. Here again two positions a and b resulted,

Table 3. Structure of the thiophene-argon complex. $r(CM_{mol}-Ar)$ denotes the distance between the center of mass of the thiophene molecule and the argon atom. ∢ (Ar, CM_{mol}, S) represents the angle between the axes from the center of mass of thiophene towards the sulfur atom (x-axis) and the argon atom. ∢ (z, Ar) describes the angle between the z-axis and the $CM_{mol}-Ar$ direction. x_{Ar}, y_{Ar}, z_{Ar} are the coordinates of the argon atom and $x_{CM(CP)}$, $y_{CM(CP)}$, $z_{CM(CP)}$ are the coordinates of the center of mass of the complex in the thiophene system. $r(CM_{CP}-S)$ is the distance between the sulfur atom and the center of mass of the complex. "a" and "b" designate the two possible positions of the argon atom. Δ gives the difference between the direct derivation of $r(CM_{CP}-S)$ by the sulfur substitution in the complex and the r_0- or the r_s-structure values derived from the "argon-substitution". The number of digits does not reflect the methodological error.

Position	r_0-Structure		r_s-Structure (argon subst.)		r_s-Structure (sulfur Subst.)
	a	b	a	b	
$r(CM_{mol}-Ar)/Å$	3.623	3.627	3.625		–
∢ (Ar, CM_{mol}, S)/°	97.293	82.297	95.939	84.061	–
∢ (z, Ar)/°	−7.293	7.703	−5.939	5.939	–
$x_{Ar}/Å$	−0.460	0.486	−0.376	0.376	–
$y_{Ar}/Å$	0	0	0	0	–
$z_{Ar}/Å$	±3.594	±3.594	±3.594		–
$x_{CM(CP)}/Å$	−0.148	0.157	−0.121	0.121	–
$y_{CM(CP)}/Å$	0	0	0	0	–
$z_{CM(CP)}/Å$	±1.159	±1.159	±1.163	±1.163	–
$r(CM_{CP}-S)/Å$	1.735	1.522	1.716	1.547	1.688
$\Delta/Å$	0.048	−0.1657	0.028	−0.141	0.0

listed in the third and fourth column of Table 3. The other entries of Table 3 are derived with the help of the given structure of thiophene. It should be pointed out that the second procedure will not compensate vibrational effects by the difference of moments of inertia in the usual way, as a zero mass atom does not contribute to vibrations. The results should be considered therefore with caution. In a third procedure we calculated the distance $r(\mathrm{CM_{CP}}-\mathrm{S})$ between the sulfur atom and the center of mass of the complex $\mathrm{CM_{CP}}$ by substituting the ^{32}S by a ^{34}S atom in the thiophene-argon complex [14]. The result is given in the last column of Table 3 and may be compared to the values derived from the preceding calculations. In the last row of Table 3 the differences between the derived distance by the sulfur substitution and the results for the two positions are given. The comparison shows that structure "*a*" may be of physical significance. As the methodological errors are rather uncertain, the statement is not absolutely strict. The argon atom seems to be shifted away from the sulfur atom. It must be mentioned that for the furane-argon complex Kukolich derived in an erratum [4] that the argon atom is shifted towards the oxygen.

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