The Rotational Spectrum of the Fluorobenzene-Argon Van der Waals Complex

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The rotational spectrum of the fluorobenzene-argon complex has been studied in the microwave region between 7 and 18 GHz using a pulsed molecular beam microwave Fourier transform spectrometer. The rotational constants were found to be $A=1811.81369(11)$ MHz, $B=1105.12965(15)$ MHz, $C=901.84281(5)$ MHz, the centrifugal distortion constants are $\Delta_J = 2.6886(17)$ kHz, $\Delta_{JK}= 8.3761(52)$ kHz, $\Delta_K = -8.278(5)$ kHz, $\delta_J = 0.65993(72)$ kHz, and $\delta_K = 6.013(11)$ kHz. The argon atom is placed 3.55 Å above the ring plane.

Introduction

The benzene-argon complex has been studied by Weber et al. [1] using mass-selected resonance-enhanced two-photon ionization and by Brupbacher et al. [2] by means of a pulsed molecular beam microwave Fourier transform (MB-MWFT) spectrometer. Both groups found the complex to be a symmetric top belonging to the point group C_{6v} with the argon atom located 3.582 resp. 3.53 Å above the ring plane. These results induced us to find out how much the position of the argon atom would be changed if one hydrogen atom of the benzene molecule is substituted by a fluorine atom. The fluorobenzene-argon complex has already been studied by different authors [3–6], but no information about the structure of the complex has been reported. Mons and Le Calvé [7] used theoretical methods to obtain structural data.

Experimental

All spectra were taken using our MB-MWFT spectrometer [8] in the range from 7 to 18 GHz. For highest resolution and sensitivity the nozzle was mounted in such a way that the molecular beam propagates along the axis of the cavity from one mirror to the other [9]. Gas mixtures containing 1% fluorobenzene (Aldrich, Steinheim) in argon and a stagnation pressure of 50 kPa (0.5 atm) were used throughout.

Spectral Analysis

We started our investigations with the prediction of rotational constants. We assumed that the geometry of the fluorobenzene molecule would be unchanged in the complex and the position of the argon atom would be essentially the same as in the benzene-argon complex. With the r_0-structure of fluorobenzene as determined by Doraiswamy and Sharma [10] and the argon atom located in a distance of 3.55 Å above the center point of the ring (i.e. on the half distance between C_1 and C_4), we found the rotational constants to be $A=1.824$ MHz, $B=1.095$ MHz, and $C=0.902$ MHz. We further assumed, that the total dipole moment would be about $\mu=1.7$ D. This is the same as in fluorobenzene [11] since polarization effects were expected to contribute only on the order of the dipole moment of the benzene-argon complex, which is 0.1 D [2]. Due to the rotation of the principal axes the total dipole moment of the complex has no longer only an *a*-component as in fluorobenzene. Instead, an *a*-component of $\mu_a=0.5$ D and a *b*-component of $\mu_b=1.5$ D should cause a weak *a*-type and a strong *b*-type spectrum.

We started our search by scanning the range from 9.6 to 10.6 GHz where the automatic operation of the spectrometer [8] again turned out to be very helpful. Four lines were found and assigned to the complex. Especially the doublett $3_{31}-2_{20}$, $3_{30}-2_{21}$ at 10.046 and 10.088 GHz was very characteristic and made the assignment easy. Together with the two other lines $4_{23}-3_{12}$ and $5_{15}-4_{04}$ at 9.839 and 9.606 GHz a least-squares fit yielded improved rotational constants. With a new prediction 17 more *b*-type and one *a*-type

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Table 1. Rotational transitions of the fluorobenzene-argon complex. ν_{obs} = observed frequency (GHz), $\Delta\nu$ = observed minus calculated frequency (kHz) from the least-squares fit.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{obs}	$\Delta\nu$
3	3	1	2	2	0	10.0460227	0.0
3	3	0	2	2	1	10.0884011	−0.0
4	3	2	3	2	1	11.9727251	−0.5
4	2	3	3	1	2	9.8387022	0.8
4	3	1	3	2	2	12.1849970	−0.3
4	4	1	3	3	0	13.6885105	0.1
4	4	0	3	3	1	13.6934543	0.1
4	1	4	3	0	3	7.9148649	−0.5
5	1	5	4	0	4	9.6064434	−0.1
5	2	4	4	1	3	11.4451072	0.5
5	0	5	4	1	4	9.2923775	−0.2
5	3	2	4	2	3	14.3980023	0.1
5	3	3	4	2	2	13.7795688	−0.1
6	2	5	5	1	4	12.9904334	−0.3
6	1	6	5	0	5	11.3339928	0.1
6	0	6	5	1	5	11.1750068	−0.0
6	1	5	5	2	4	11.1166661	0.4
7	1	7	6	0	6	13.0943906	0.1
7	2	6	6	1	5	14.5234438	0.0
7	0	7	6	1	6	13.0190276	−0.0
7	1	6	6	2	5	13.3046780	−0.3
5	0	5	4	0	4	9.4991481	−0.0

Table 2. Rotational constants and quartic centrifugal distortion constants of the fluorobenzene-argon complex. Watson's A-reduction and the I^r-representation were used. N = number of the lines in the fit, σ = standard deviation.

A	1.81181369(11)	GHz	$N = 22$
B	1.10512965(15)	GHz	$\sigma = 0.38$ kHz
C	0.90184281(5)	GHz	
Δ_J	2.6886(17)	kHz	
Δ_{JK}	8.3761(52)	kHz	
Δ_K	−8.278(5)	kHz	
δ_J	0.65993(72)	kHz	
δ_K	6.013(11)	kHz	

transition were found. All measured lines are compiled in Table 1. Due to the high resolution of the spectrometer it was possible to determine all quartic centrifugal distortion constants with a surprisingly good accuracy despite the fact that only lines up to $J=7$ were measured. The results of the least-squares fit are presented in Table 2, the corresponding correlation and freedom-cofreedom matrices are given in Table 3. For the interpretation of the freedom-cofreedom matrix see [12, 13].

Table 3. Correlation matrix and freedom-cofreedom matrix from the least-squares fit corresponding to the parameters given in Table 1. For details of the freedom-cofreedom matrix see [12]. Its diagonal elements are the freedom coefficients as defined by Femenias [13].

Correlation matrix

	A	B	C	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K
A	1.000							
B	0.066	1.000						
C	−0.366	−0.361	1.000					
Δ_J	0.009	0.978	−0.284	1.000				
Δ_{JK}	0.378	−0.823	0.272	−0.839	1.000			
Δ_K	0.468	0.669	−0.522	0.611	−0.554	1.000		
δ_J	0.109	0.959	−0.529	0.935	−0.783	0.662	1.000	
δ_K	0.181	0.888	−0.531	0.913	−0.725	0.635	0.883	1.000

Freedom-cofreedom matrix

	A	B	C	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K
A	0.210							
B	0.999	0.148						
C	0.946	0.961	0.225					
Δ_J	0.976	0.430	0.640	0.066				
Δ_{JK}	0.541	0.753	0.933	0.690	0.139			
Δ_K	0.599	0.858	0.919	0.876	0.650	0.262		
δ_J	0.991	0.529	0.635	0.483	0.770	0.865	0.126	
δ_K	0.992	0.666	0.638	0.440	0.821	0.879	0.565	0.154

Table 4. r_0 coordinates (Å) of the fluorobenzene molecule as determined by Doraiswamy and Sharma [10]. The observed and calculated rotational constants (GHz) of fluorobenzene are also given.

Atom	b	a	c
C_1	0.0	−0.8528	0.0
$C_{2/6}$	±1.2178	−0.1937	0.0
$C_{3/5}$	±1.2093	1.2027	0.0
C_4	0.0	1.9045	0.0
F_1		−2.2068	0.0
$H_{2/6}$	±2.1378	−0.7613	0.0
$H_{3/5}$	±2.1513	1.7371	0.0
H_4	0.0	2.9845	0.0
	obs.	calc.	obs.-calc.
A	5.66354	5.66366	−0.00012
B	2.57064	2.57035	0.00029
C	1.76794	1.76798	−0.00004

Discussion

Our experiments and the spectral analysis provided us with three rotational constants and five quartic centrifugal distortion constants of the complex. The rotational constants are in good agreement with our initial guess. We used them to fit the displacement of the argon atom from the center of mass of the fluorobenzene molecule. With the r_0-structure of fluorobenzene as given by Doraiswamy and Sharma [10] (Table 4) we found that the argon atom is placed 3.553 Å abvove the ring. It is shifted ±0.460 Å along the C_1-C_4 axis referring to the center of mass of the

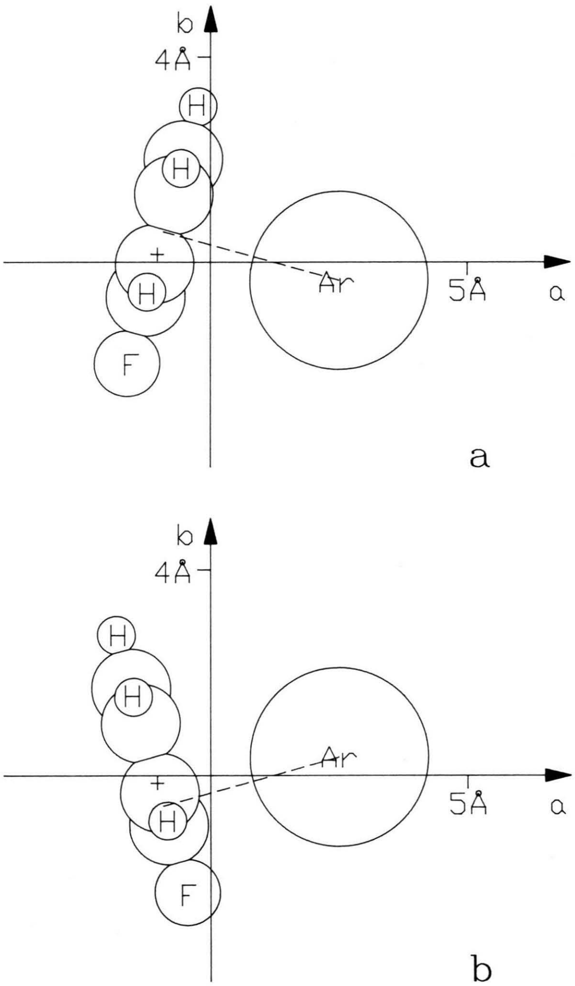

Fig. 1. Schematic diagram of both possible structures of the fluorobenzene-argon complex drawn in the *a*, *b*-plane. The corresponding r_0 coordinates are given in Table 5. The center of mass of the fluorobenzene molecule is marked by "+".

fluorobenzene molecule. It should be noted that the sign of the displacement is not determinable. Both possibilities are mathematically equivalent (see Fig. 1 a and b). Since theoretical calculations [7] have shown that the argon atom should be placed 3.48 Å above the ring and displaced only 0.18 Å from the center of the ring along the C_1-C_4 axis towards the fluorine atom we are convinced that only the structure given in Fig. 1 a is of physical significance. In the second possible structure shown in Fig. 1 b the shift of the argon atom along the C_1-C_4 axis appears too large. r_0 coordinates of the fluorobenzene-argon complex are given in Table 5. There is a deviation of 1.9 resp. 2.8 MHz between the observed and calculated rotational constants *B* and *C*. This could be due to a rather floppy structure of the molecule. A slight change of the geometry of the fluorobenzene molecule could also explain this deviation.

Table 5. r_0 coordinates (Å) of both possible structures of the fluorobenzene-argon complex. Observed and fitted rotational constants (GHz) are also given.

Atom	*a*	*b*	*c*
Structure a			
C_1	−1.2691	−0.6725	0.0
$C_{2/6}$	−1.0934	−0.0372	±1.2178
$C_{3/5}$	−0.7211	1.3087	±1.2093
C_4	−0.5340	1.9851	0.0
F	−1.6300	−1.9775	0.0
$H_{2/6}$	−1.2447	−0.5843	±2.1378
$H_{3/5}$	−0.5787	1.8237	±2.1513
H_4	−0.2461	3.0260	0.0
Ar	2.5043	−0.3565	0.0
Structure b			
C_1	−0.8150	−0.9691	0.0
$C_{2/6}$	−0.9907	−0.3339	±1.2178
$C_{3/5}$	−1.3630	1.0120	±1.2093
C_4	−1.5501	1.6884	0.0
F	−0.4541	−2.2741	0.0
$H_{2/6}$	−0.8394	−0.8809	±2.1378
$H_{3/5}$	−1.5055	1.5271	±2.1513
H_4	−1.8380	2.7293	0.0
Ar	2.5043	0.3565	0.0
	obs.	calc.	obs.-calc.
A	1.81181	1.81111	0.00070
B	1.10513	1.10325	0.00188
C	0.90184	0.90463	−0.00279

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