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# Rotational spectra of isotopic furan– $(argon)_n$ , n = 1,2, complexes and their vibrationally averaged structures

R.M. Spycher, L. Hausherr-Primo, G. Grassi, A. Bauder\*

Laboratorium für Physikalische Chemie, Eidgenössiche Technische Hochschule, CH-8092 Zürich, Switzerland

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#### Abstract

Pulsed nozzle Fourier transform microwave spectroscopy has been used to observe the rotational spectrum of the furan-3,4- $d_2$ -(argon)<sub>2</sub> van der Waals complex. The rotational spectra of the furan-3-d-, furan-3,4- $d_2$ -, and furan- $d_4$ - argon complexes have been measured in addition to the two previously measured isotopomers furan- and furan-2-d- argon. Rotational and quartic centrifugal distortion constants have been fitted for each isotopomer. Deuterium quad-rupole coupling constants have been determined for the furan-3-d-argon complex from hyperfine splittings of the rotational transitions. A model considering the effects of large-amplitude van der Waals vibrations has been used for the determination of the intermolecular structural parameters. Argon has been located at a distance R = 3.539(2) Å from the center-of-mass of furan for the furan-argon complex. Argon has been found shifted towards the oxygen including an angle  $\theta = 9.7(2)^{\circ}$  between R and the principal axis c of furan. In the furan-(argon)<sub>2</sub> complex, the two argon atoms assume symmetrical positions above and below the plane of furan with R and  $\theta$  almost unchanged compared with the furan-argon complex.

#### 1. Introduction

A number of rotational spectra for complexes between an aromatic molecule and rare gas atoms have been observed over the last decade. The first example studied was the furan-argon complex [1,2]. More recently, the pyrrole-argon [3], pyridineargon, and pyridine-krypton [4] complexes were measured. The permanent electric dipole moments of the furan- and pyrrole-argon complexes exhibited specific shifts with respect to the dipole moments of the aromatic monomers [5]. The changes were attributed to the induced dipole moment in argon. Two-photon resonance enhanced multiphoton

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ionization (REMPI) spectra with rotational resolution provided the first data on the benzene-argon complex [6]. The complex is slightly polar owing to mutual polarization although both monomers of this complex have no permanent dipole moment. The pure rotational spectrum of benzene-argon was observed later in the microwave range [7]. The dipole moment of the complex was estimated from Stark splittings. The complexes of benzene with the other rare gas atoms, except helium, were also investigated using REMPI spectroscopy with rotational resolution [8,9]. The microwave spectrum of benzene-krypton was reported recently including the electric dipole moment and the <sup>83</sup>Kr quadrupole coupling constant [10].

<sup>\*</sup> Corresponding author.

The formation of complexes between an aromatic molecule and rare gas atoms is not restricted to a single rare gas atom. An almost unlimited number of rare gas atoms may surround the aromatic molecule leading finally to a microdroplet with the aromatic molecule dissolved in it [11-14]. However, detailed spectroscopic data can only be expected for complexes with few rare gas atoms. A benzene-(argon)<sub>2</sub> complex was recently measured with rotationally resolved REMPI spectroscopy [15]. Subsequently, the rotational spectra of furan-(argon)<sub>2</sub> [16] and pyridine–(argon)<sub>2</sub> [17] were assigned and analyzed in the microwave range. In all these complexes, the argon atoms occupied symmetrical positions above and below the plane of the aromatic molecule. Two or more isomers were assigned to the observed bands in vibrationally resolved **REMPI** spectra of complexes with more than one argon atom [18]. The isomers were characterized with respect to the number of argon atoms attached to either side of the aromatic ring plane. If two argon atoms were bound to the same side of the ring plane as an argon dimer, theoretical calculations with a simple Lennard-Jones potential indicated several almost equally stable conformers to be present separated by small barriers [19]. This fact would lead to unusual and complicated rotational spectra which have not yet been investigated.

Large-amplitude intermolecular vibrations occur between the subunits of the aromatic moleculerare gas complexes. These van der Waals vibrations must be considered for the determination of the structure. Isotopically substituted species are necessary for the complete determination of the intermolecular structural parameters [2,16]. At the same time, they help in reducing the effects of the large-amplitude vibrations on the structure. Klots et al. [4] proposed a novel method for the structure determination which explicitly accounted for the bending vibrations between the aromatic molecule and the rare gas. Some problems with their preliminary data on the furan-argon complex prompted us to further investigate this, as well as the furan-(argon)<sub>2</sub> complex.

We report here the measurements of the rotational spectra for additional isotopic species of the complexes of furan with one or two argon atoms. The spectroscopic constants have been used to derive a vibrationally averaged structure of the complexes. The method for the structure determination has also been extended to the complexes with two argon atoms [17].

# 2. Experimental

# 2.1. Spectrometer

The design of our pulsed nozzle Fourier transform microwave spectrometer is similar to the instrument described by Balle and Flygare [20]. The details were reported previously [16,21] and only a short description of the operating conditions is given here. In order to improve the sensitivity, four microwave pulses of 1  $\mu$ s duration and a power of 0.5 mW were applied to one gas pulse propagating perpendicularly to the cavity axis. The polarization decay signals of the complexes were coadded from a few hundred gas pulses digitized at a rate of 5 MHz for 512 channels with an 8-bit analog-to-digital converter. Peak frequencies of rotational transitions were interpolated to an accuracy of 5 kHz from the Fourier transformed power spectrum with a channel separation of 38 kHz. At least two measurements were performed with two slightly different microwave frequencies. Complexes were formed by expanding a gas mixture of 0.5% furan in argon at a total pressure of 3 bar through a nozzle of 0.5 mm diameter into the vacuum chamber using a pulsed valve (General Valve, Series 9).

#### 2.2. Chemicals

#### 2.2.1. Furan-3-d

3-Bromofuran (Aldrich, 97%) was dissolved in tetrahydrofuran and reacted at  $-75 \pm 5^{\circ}$ C with *n*-butyllithium (Aldrich, 2 M in cyclohexane). The lithium compound was hydrolyzed at  $-65 \pm 5^{\circ}$ C with methanol-OD (Ciba-Geigy, 99.5%) [22]. The raw product was separated by distillation through a Spaltrohr column. It was purified by preparative gas chromatography to 99.7%. It contained 93% furan-3-*d*, 6% furan, and less than 1% furan-*d*<sub>2</sub> as

Table 1 Observed rotational transition frequencies (MHz) of the furan- $3,4-d_2$ -(argon)<sub>2</sub> complex

$J_{K_a'K_c'}' - J_{K_a''K_c''}''$	$ u_{ m obs}$	$\Delta  u^{a}$	
$5_{15}-4_{04}$	8093.070	-1	
$6_{16} - 5_{05}$	9038.743	-1	
$6_{24} - 6_{15}$	9774.821	1	
$5_{23} - 5_{14}$	9803.151	-3	
$3_{22} - 3_{13}$	9904.540	-9	
423-414	9924.076	3	
$5_{24} - 5_{15}$	9948.485	1	
$6_{25} - 6_{16}$	9977.787	2	
$7_{17} - 6_{06}$	9979.709	2	
$2_{21} - 1_{10}$	11819.980	0	
$2_{20} - 1_{11}$	11829.754	9	
$4_{22} - 3_{13}$	13803.891	-4	
$5_{23} - 4_{14}$	14798.487	-1	

<sup>a</sup>  $\Delta \nu = \nu_{\rm obs} - \nu_{\rm calc}$  in kHz.

determined from <sup>1</sup>H NMR and mass spectroscopic measurements.

#### 2.2.2. Furan-3,4-d<sub>2</sub>

2-Butyne-1,4-diol (Fluka, 98%) was dissolved in chloroform and reacted with bromine [23]. The raw product was purified by recrystallization from n-butanol. The dibromide was converted by oxidation with potassium dichromate according to the method of Gorzynski and Rewicki [24] to 3,4dibromofuran which was dissolved in tetrahydrofuran, reacted with *n*-butyllithium at  $-70 \pm 5^{\circ}$ C, and hydrolyzed with methanol-OD [22]. The resulting 3-bromofuran-4-d was isolated by distillation through a Spaltrohr column and its identity confirmed by comparison with 3-bromofuran in a gas chromatograph. It was further reacted with *n*-butyllithium observing the same conditions as above and hydrolyzed with methanol-OD. Furan-3,4- $d_2$  was obtained after distillation and preparative gas chromatography with a purity of 99.3%. It contained 70% furan-3,4-d<sub>2</sub>, 18% furan-3-d, 10% furan-2,3,4-d<sub>3</sub>, and 1% furan-2-d as determined from <sup>1</sup>H NMR and mass spectroscopic measurements.

#### 2.2.3. Furan-d<sub>4</sub>

A commercial sample of furan- $d_4$  (Aldrich, 99% D) was purified by preparative gas chromatography to more than 99.8% purity.

Table 2 Spectroscopic constants of furan– $(argon)_2$  complexes from a least-squares fit of rotational transitions<sup>a</sup>

Constant	Furan-3,4- $d_2$ -(argon) <sub>2</sub>	Furan-(argon) <sub>2</sub> <sup>t</sup>	
A	3779.7572(122)	4187.6694(17)	
В	492.2651(16)	493.8114(32)	
С	482.5208(8)	486.5645(31)	
$\Delta_I$	0.514(23)	0.4425(24)	
$\Delta_{IK}$	-0.847(60)	-1.2858(91)	
$\Delta_{\kappa}$	121.(3)	144.13(34)	
$\delta_I$	0.042(11)	0.0198(7)	
$\delta_K$	0.0 <sup>c</sup>	7.(2)	

<sup>a</sup> Rotational constants A, B and C in MHz, all other constants in kHz. Numbers in parentheses represent one standard deviation. <sup>b</sup> Ref. [16].

<sup>c</sup> Constrained to zero.

### 3. Spectral analysis and results

# 3.1. Furan-3,4- $d_2$ -(argon)<sub>2</sub>

The rotational transition frequencies of the isotopically substituted complex were predicted from a model of the structure which was previously determined for the furan-(argon)<sub>2</sub> complex [16]. The principal axis system of the complex was rotated with respect to that of the monomer. The direction of the c axis of the complex coincided with that of the monomer. The a axis of the monomer included a small angle  $\phi$  with the *b* axis of the complex. Thus the predominant component of the electric dipole moment lay in the b axis giving rise to  $\mu_b$ -type transitions. Rotational transitions were readily identified and assigned. They were much broader than those of  $furan-(argon)_2$ . The broad lineshape was attributed to unresolved nuclear quadrupole splittings of the two deuteriums. It was also responsible for a substantial decrease of the peak intensities of the observed transitions. Finally, only seven R-branch and six Q-branch transitions were measured accurately. Their frequencies are listed in Table 1.

Three rotational constants and four quartic centrifugal distortion constants were fitted to the measured transition frequencies as shown in Table 2. The centrifugal distortion constants are defined according to Watson's asymmetric reduction in the prolate  $I^r$  representation [25].



Fig. 1. Deuterium nuclear quadrupole splitting of the  $4_{23}-4_{13}$  rotational transition of furan-3-*d*-argon. The circles mark the power spectrum by transforming the 512 channels of the time domain signal. The continuous line was calculated by zero-filling in the time domain up to 4096 channels.

#### 3.2. Furan-argon isotopomers

The rotational spectra of the isotopically substituted furan-argon complexes were predicted from

#### Table 3

Observed rotational transition frequencies (MHz) of the furan-3-d-argon complex

$J_{K_a'K_c'}'-J_{K_a''K_c''}''$	F'-F''	$ u_{\rm obs}$	$\Delta \nu^{a}$
$2_{11} - 1_{01}$	3-2	8643.418	-2
$5_{24} - 5_{14}$	6-6	9606.952	0
-	5-5	9607.007	0
$4_{23} - 4_{13}$	5-5	9651.173	-0
	4-4	9651.231	-1
$4_{22} - 4_{13}$	5-5	9652.226	0
	4-4	9652.284	0
$3_{21} - 3_{12}$	4-4	9686.948	1
	3-3	9687.014	1
$2_{21} - 2_{12}$	3-3	9765.506	0
$2_{20} - 2_{12}$	3–3	9765.576	-0
$5_{23} - 5_{15}$	5-5	9870.772	- l
$5_{05} - 4_{13}$	6-5	10089.675	-2
	5–4	10089.718	-1
$5_{05} - 4_{14}$	5-4	10263.937	1
$4_{14} - 3_{13}$	5-4	10705.593	0
$4_{04} - 3_{03}$	4-3	10740.103	2
$4_{13} - 3_{12}$	5-4	10775.292	-2
$5_{23} - 4_{22}$	5-4	13425.233	1

<sup>a</sup>  $\Delta \nu = \nu_{obs} - \mu_{calc}$  in kHz.

Table 4 Observed rotational transition frequencies (MHz) of the furan- $3,4-d_2$ -argon complex

$J'_{K'_aK'_c} - J''_{K''_aK''_c}$	$\nu_{\rm obs}$	$\Delta  u^{ m a}$	$J_{K_a'K_c'}' - J_{K_a''K_c''}''$	$ u_{ m obs}$	$\Delta \nu^{a}$
$3_{03} - 2_{02}$	7947.359	-4	523-422	13243.171	3
826-817	9111.942	$^{-2}$	$5_{05} - 4_{04}$	13243.919	-2
$3_{22} - 3_{13}$	9229.607	-5	$5_{14} - 4_{13}$	13257.444	-2
$4_{23} - 4_{14}$	9239.957	3	$9_{19} - 8_{26}$	14495.799	-1
$7_{17} - 6_{24}$	9249.994	3	$2_{20} - 1_{11}$	14514.732	1
$5_{24} - 5_{15}$	9252.872	4	$7_{07} - 6_{16}$	15524.783	-0
$6_{25} - 6_{16}$	9268.349	1	$6_{16} - 5_{15}$	15874.829	-1
$7_{26} - 7_{17}$	9286.381	-1	$6_{33} - 5_{32}$	15888.841	3
827-818	9306.956	-3	$6_{25} - 5_{24}$	15890.311	2
$4_{14} - 3_{13}$	10584.800	1	$6_{24} - 5_{23}$	15890.559	1
$4_{04} - 3_{03}$	10595.894	-1	$6_{06} - 6_{05}$	15891.316	-0
$4_{13} - 3_{12}$	10606.693	-3	$6_{15} - 5_{14}$	15907.577	3
$5_{15} - 4_{14}$	13230.111	0	$5_{15} - 4_{04}$	16273.578	-0
$5_{24} - 4_{23}$	13243.025	-0	$3_{21} - 2_{12}$	17168.664	2

<sup>a</sup>  $\Delta \nu = \nu_{obs} - \nu_{calc}$  in kHz.

the known structure of the complex [2]. It should be pointed out again that the orientation of the principal axis system  $a^{M}, b^{M}, c^{M}$  changed between the different isotopomers of furan. Unrelated changes occurred in the corresponding complexes.

Rotational transitions of the furan-3-d-argon complex were first observed as weak lines from the small contamination of the furan-3,4- $d_2$ sample with furan-3-d. Because the permanent dipole moment of this complex has components in all three directions of the principal axis system,  $\mu_{a}$ ,  $\mu_{b}$ , and  $\mu_{c}$ -type transitions were observed. They showed mostly resolvable splittings owing to the deuterium nuclear quadrupole coupling. A typical example is shown in Fig. 1. Often some of the quadrupole components coincided within the observed linewidths and the splitting pattern degenerated typically into a doublet. In this situation, only the frequency of the clearly resolved quadrupole component was measured accurately. The frequencies of 19 quadrupole components from 14 pure rotational transitions are listed in Table 3. Three rotational constants, four quartic centrifugal distortion constants and two independent diagonal quadrupole coupling constants of the deuterium nucleus were fitted simultaneously from this set of frequencies. The results are given in Table 6.

The unresolved quadrupole splittings due to the

Table 5 Observed rotational transition frequencies (MHz) of the furan $d_4$ -argon complex

$\frac{J'_{K'_aK'_c}-J''_{K''_aK''_c}}{-}$	$ u_{\rm obs}$	$\Delta \nu^{a}$	
$2_{11} - 1_{01}$	7973.859	8	
$4_{23} - 4_{13}$	8143.181	-3	
$5_{05} - 4_{13}$	10165.636	6	
$4_{14} - 3_{13}$	10366.725	2	
$4_{04} - 3_{03}$	10402.325	-3	
$4_{13} - 3_{12}$	10438.963	-7	
$3_{12} - 2_{02}$	10601.587	4	
$5_{15} - 4_{14}$	12957.409	-1	
$5_{05} - 4_{04}$	13001.409	-1	
$5_{24} - 4_{23}$	13002.021	$^{-2}$	
$5_{23} - 4_{22}$	13003.803	-2	
$5_{14} - 4_{13}$	13047.706	-4	
$4_{13} - 3_{03}$	13238.107	-1	
$4_{31} - 4_{23}$	13723.048	1	
$6_{16} - 5_{15}$	15547.432	-3	
$6_{06} - 5_{05}$	15599.496	2	
$6_{25} - 5_{24}$	15601.047	2	
$6_{24} - 5_{23}$	15604.164	1	
$6_{15} - 5_{14}$	15655.781	1	
$5_{14} - 4_{04}$	15883.491	1	

<sup>a</sup>  $\Delta \nu = \nu_{obs} - \nu_{calc}$  in kHz.

two deuterium nuclei broadened the rotational transitions of the symmetrically substituted furan-3,4- $d_2$ -argon complex. Because of the reduced peak intensity, only the stronger transitions were measured accurately. The frequencies of 15  $\mu_a$ - and 13  $\mu_b$ -type transitions are listed in Table 4. Three rotational constants and all five centrifugal distortion constants were determined in a leastsquares fit from these frequencies. The results are included in Table 6.

The rotational transitions of the furan- $d_4$ -argon complex turned out to be weak and extremely broad with linewidths at FWHM up to 50 kHz. The broadening was attributed to the unresolved quadrupole splittings of four deuterium nuclei. Finally, 13  $\mu_a$ -type and 7  $\mu_c$ -type transitions were identified. Their accurately measured frequencies are collected in Table 5. Three rotational constants and four centrifugal distortion constants determined in a least squares fit are given in Table 6.

# 3.3. Furan-3,4-d<sub>2</sub> monomer

The moments of inertia of furan-3,4- $d_2$  were needed for the determination of the structures of the corresponding complexes with argon. The rotational spectrum of this isotopomer of furan has never been measured so far. Initially, three rotational transitions were identified using the molecular beam spectrometer. Based on their frequencies, transitions were predicted in the frequency range between 18 and 26 GHz. Fourteen additional transitions were observed with a conventional Stark spectrometer in the static gas at room temperature [17]. A list of the measured  $\mu_a$ -type transitions is

Table 6

Spectroscopic constants of furan-argon complexes from least-squares fits of rotational transitions<sup>a</sup>

Constant	Furan-argon <sup>b</sup>	Furan-3-d-argon	Furan-3,4- <i>d</i> <sub>2</sub> -argon	Furan-d <sub>4</sub> -argon	
A	4802.3467(9)	4589.2824(19)	4395.9201(39)	4045.3786(18)	-
В	1362.6089(3)	1351.4800(4)	1327.4329(52)	1309.5822(5)	
С	1360.2930(3)	1334.0455(5)	1321.8765(49)	1291.5181(6)	
$\Delta_J$	5.284(6)	5.074(11)	4.966(3)	4.617(7)	
$\Delta_{IK}$	29.343(12)	27.504(21)	25.634(16)	24.308(66)	
$\Delta_{\kappa}$	-22.74(19)	-19.50(41)	-19.22(83)	-20.43(54)	
δ	-0.0420(13)	0.0735(34)	0.0976(17)	0.0141(52)	
$\delta_K$	0.0 <sup>c</sup>	0.0 <sup>c</sup>	17.(3)	0.0 <sup>c</sup>	
$\chi_{aa}$	_	-85.(6)	_	_	
Xhh	_	177.(5)	_	_	
Xcc	-	-92.(5)	_	_	

<sup>a</sup> Rotational constants A, B and C in MHz, all other constants in kHz. Numbers in parentheses represent one standard deviation.

<sup>b</sup> Ref. [2].

<sup>c</sup> Constrained to zero.

Table 7 Observed rotational transition frequencies (MHz) of the furan-3,4-d<sub>2</sub> monomer

$J_{K_a'K_c'}'-J_{K_a''K_c''}''$	$ u_{\rm obs}$	$\Delta  u^{ m a}$	
$\overline{3_{21}-3_{22}}$	11146.223	-6	
$2_{11} - 2_{12}$	11964.818	3	
$1_{01} - 0_{00}$	12509.458	3	
$6_{42} - 6_{43}$	18933.597	3	
$5_{51} - 5_{32}$	19101.215	-2	
532-533	20019.148	-3	
422-423	20730.803	1	
$2_{12} - 1_{11}$	21030.601	0	
$3_{12} - 3_{13}$	21120.897	-2	
$3_{22} - 3_{03}$	21405.664	3	
$2_{02} - 1_{01}$	21544.352	-2	
$4_{32} - 4_{13}$	21575.210	1	
$5_{42} - 5_{23}$	21936.109	-1	
$6_{61} - 6_{42}$	22487.764	1	
652-633	22604.633	0	
$7_{62} - 7_{43}$	23729.974	-1	
872-853	25483.989	1	

<sup>a</sup>  $\Delta \nu = \nu_{obs} - \nu_{calc}$  in kHz.

given in Table 7. In a least-squares fit, three rotational constants and four centrifugal distortion constants were obtained as shown in Table 8. The planarity conditions were invoked for the reduction to only four quartic centrifugal distortion constants [26].

### 4. Vibrationally averaged molecular structure

The rare gas atoms were located above or symmetrically on both sides of the plane of the aromatic molecules for all previously studied

Table 8

Spectroscopic constants of the furan-3,4- $d_2$  monomer from a least-squares fit of rotational transitions<sup>4</sup>

A	8819.6010(7)	
В	8248.8750(16)	
С	4260.5864(9)	
$ au_{aaaa}$	-14.17(65)	
$\tau_{bbbb}$	-12.72(60)	
$\tau_{aabb}$	-6.(2)	
$\tau_{abab}$	-3.6(6)	

<sup>a</sup> Rotational constants A, B and C in MHz, centrifugal distortion constants  $\tau$  in kHz. Numbers in parentheses represent one standard deviation.



Fig. 2. Model of the furan-argon and furan-(argon)<sub>2</sub> complexes with the definition of the intermolecular structural parameters R and  $\theta$  and the principal axis systems for the furan monomer  $(x^M, y^M, z^M)$  and the complex  $(x^C, y^C, z^C)$ .

complexes [1-10,15-17]. The structure of furan- $(\operatorname{argon})_n$ , n = 1, 2, complexes will be described by two structural parameters, the distance R between the center-of-mass of furan and argon and the angle  $\theta$  between R and the principal axis c of furan as depicted in Fig. 2. Argon atoms lie in a symmetry plane perpendicular to the ring plane for aromatic molecules with  $C_{2v}$  symmetry. In furan-(argon)<sub>2</sub>, they are related by symmetry such that the distance of the second is R and the angle is the supplement of  $\theta$ . It must be pointed out that the conventional labeling of the inertial axes changes with respect to those of the parent molecule between different isotopomers of the monomer and of the corresponding complexes. The principal axis system of the monomer will be denoted by  $x^{M}, y^{M}, z^{M}$  and that of the complex by  $x^{C}, y^{C}, z^{C}$ irrespective of the order of the rotational constants.

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Isotopomer	x	у	Z	P <sub>x</sub>	<b>P</b> <sub>y</sub>	<i>P</i> <sub>2</sub>	Ref.
Furan	а	ь	с	54.6792	53.5199	-0.0244	[27]
Furan–Ar	с	b	а	52.3019	52.9340	318.5886	[1]
Furan-Ar <sub>2</sub>	b	с	а	67.9628	52.7199	970.7054	[16]
Furan-3,4- $d_2$	а	b	с	61.2909	57.3263	-0.0244	This work
Furan-3,4- $d_2$ -Ar	b	С	а	58.2829	56.6826	324.0365	This work
Furan-3, $4 - d_2 - Ar_2$	b	с	а	77.2879	56.4192	970.1511	This work
Furan-d <sub>4</sub>	b	а	с	62.7522	65.7584	-0.0228	[27]
Furan-d <sub>4</sub> -Ar	с	b	а	59.7654	65.1614	326.1442	This work

Table 9 Planar moments  $(uÅ^2)$  of the observed isotopomers of furan and of furan-(argon)<sub>n</sub>, n = 1, 2, complexes

The principal axis  $y^{C}$  is perpendicular to the symmetry plane of the complex and is parallel to  $y^{M}$ . The axis  $z^{M}$  is perpendicular to the ring plane with  $z^{C}$  rotated by a small angle  $\gamma$ .

The structure of furan is assumed to remain unchanged when the complex with one or two argon atoms is formed. The moments of inertia of the isotopic furan monomers in the ground vibrational state will be used for the calculation of the structure of the complexes. The largeamplitude intermolecular motions between furan and argon cannot be neglected for the structure determinations. This is clearly seen from the planar moment of inertia  $P_y$  of the complex and of the furan monomer. Planar moments of inertia are defined as

$$P_{\xi} = (I_{\zeta} + I_{\eta} - I_{\xi})/2$$
  
 $\xi, \zeta, n = x, y, z$  and cyclic permutations (1)

from the moments of inertia  $I_{\xi}$ . In the complex,



Fig. 3. Model for the intermolecular bending motion between furan and argon.

only the nuclei of the monomer contribute to  $P_y$  as argon is located on the symmetry plane xz. A comparison of  $P_y$  between monomer and complex for different isotopomers is given in Table 9. The values of  $P_y$  for the listed isotopomers of furanargon are on the average  $0.61 \pm 0.03 \text{ uÅ}^2$  smaller than those of the corresponding monomer. Similarly for furan-(argon)<sub>2</sub>, the values for the complexes are on the average  $0.85 \pm 0.05 \text{ uÅ}^2$  smaller than those of the monomers. This reduction is attributed to a bending motion of furan around its  $x^M$  axis that shortens the effective distance of the nuclei perpendicular to the inertial plane xz.

A novel method for the structure determination of aromatic molecule– $(rare gas)_n$ , n = 1,2, complexes was recently developed and tested for pyridine– $(argon)_n$ , n = 1, 2, complexes [17]. The large-amplitude bending of argon above the ring plane was considered explicitly. A similar model was introduced earlier by Klots et al. [4]. In order to approximately fulfil the Eckart conditions for the bending, the aromatic molecule was rotated at its center-of-mass around  $x^{M}$  and  $y^{M}$  by the angles  $\alpha_x$  and  $\alpha_y$ , respectively. The vibrationally averaged angles  $\langle \alpha_x \rangle$  and  $\langle \alpha_y \rangle$  were assumed to be equal and their difference was neglected in this model. The bending was thus treated as a two-dimensional degenerate vibration. The motion of furan is described first by a rotation with the angle  $\varphi$  around  $z^{M}$ , then with the angle  $\alpha$  around  $x^{M}$  followed by a rotation with the angle  $-\varphi$  around  $z^{M}$ as shown schematically in Fig. 3. The inertia tensor of furan which is transformed by the product of these three rotations becomes a function of the

Table 10 Intermolecular structural parameters of furan– $(argon)_n$ , n = 1, 2, complexes from fits of all observed isotopomers<sup>a</sup>

Isotopomer	R	θ	$\langle lpha  angle$	$\gamma$
Furan-Ar	3.5410	9.66	8.51	11.55
Furan-3,4-d2-Ar	3.5486	10.33	8.62	12.59
Furan- $d_4$ -Ar	3.5425	10.37	7.74	12.70
Furan-Ar <sub>2</sub>	3.5368	10.09	9.96	0.00
Furan-3,4- $d_2$ -Ar <sub>2</sub>	3.5454	10.96	10.25	0.00

<sup>a</sup> The structural parameters are defined in the text (see Fig. 2). Distances are given in Ångströms and angles in degrees.

angles  $\alpha$  and  $\varphi$ . It is then averaged over  $\varphi$ . Its elements are expressed explicitly as vibrational averages of  $\alpha$  in the form

$$\langle I_{xx}^{\mathbf{M}} \rangle = I_{xx}^{\mathbf{M}} \langle 1 + \frac{1}{2} \sin^{2} \alpha \rangle - P_{z}^{\mathbf{M}} \langle \sin^{2} \alpha \rangle - \frac{1}{2} (I_{xx}^{\mathbf{M}} - I_{yy}^{\mathbf{M}}) \langle \sin^{2} \alpha + \sin^{4} (\alpha/2) \rangle \langle I_{yy}^{\mathbf{M}} \rangle = I_{yy}^{\mathbf{M}} \langle 1 + \frac{1}{2} \sin^{2} \alpha \rangle - P_{z}^{\mathbf{M}} \langle \sin^{2} \alpha \rangle + \frac{1}{2} (I_{xx}^{\mathbf{M}} - I_{yy}^{\mathbf{M}}) \langle \sin^{2} \alpha + \sin^{4} (\alpha/2) \rangle \langle I_{zz}^{\mathbf{M}} \rangle = I_{zz}^{\mathbf{M}} \langle 1 - \frac{1}{2} \sin^{2} \alpha \rangle + P_{z}^{\mathbf{M}} \langle \sin^{2} \alpha \rangle$$
(2)

The inertia tensor of the furan-argon complex is calculated in a coordinate system parallel to  $x^{M}, y^{M}, z^{M}$  but shifted to the center-of-mass of the complex

$$I'_{xx} = \langle I^{M}_{xx} \rangle + \mu R^{2} \cos^{2} \theta$$

$$I'_{yy} = \langle I^{M}_{yy} \rangle + \mu R^{2}$$

$$I'_{zz} = \langle I^{M}_{zz} \rangle + \mu R^{2} \sin^{2} \theta$$

$$I'_{xz} = \mu R^{2} \cos \theta \sin \theta$$
(3)

Table 11

Intermolecular structural parameters referring to the parent species of furan- $(\operatorname{argon})_n$ , n = 1, 2, complexes corrected for center-of-mass shifts of isotopomers<sup>a</sup>

Isotopomer	R'	$\theta'$	$\langle \alpha_x \rangle = \langle \alpha_y \rangle$
Furan-Ar	3.541	9.66	6.01
Furan-3,4-d2-Ar	3.540	9.49	6.08
Furan-d <sub>4</sub> -Ar	3.537	9.91	5.47
Furan-Ar <sub>2</sub>	3.537	10.1	5.20
Furan-3,4- $d_2$ -Ar <sub>2</sub>	3.536	10.1	5.28

<sup>a</sup> The structural parameters are defined in the text. Distances are given in Ångströms and angles in degrees.

where

$$\mu = mM/(m+M)$$

is the reduced mass of the complex with m and M representing the mass of argon and of the furan monomer, respectively. Finally, the inertia tensor is transformed to the principal axis system  $x^{C}, y^{C}, z^{C}$  by diagonalization

$$I_{xx}^{C} = \frac{1}{2} (\langle I_{xx}^{M} \rangle + \langle I_{zz}^{M} \rangle + \mu R^{2}) + \frac{1}{2} (\langle I_{xx}^{M} \rangle - \langle I_{zz}^{M} \rangle + \mu R^{2} \cos 2\theta) (1 + tan^{2}2\gamma)^{\frac{1}{2}}$$

$$I_{yy}^{C} = \langle I_{yy}^{M} \rangle + \mu R^{2}$$

$$I_{zz}^{C} = \frac{1}{2} (\langle I_{xx}^{M} \rangle + \langle I_{zz}^{M} \rangle + \mu R^{2}) - \frac{1}{2} (\langle I_{xx}^{M} \rangle - \langle I_{zz}^{M} \rangle + \mu R^{2} \cos 2\theta) (1 + tan^{2}2\gamma)^{\frac{1}{2}}$$

$$(4)$$

where

$$\tan 2\gamma = 2I'_{xz}/(\langle I^{\mathbf{M}}_{zz} \rangle - \langle I^{\mathbf{M}}_{xx} \rangle - \mu R^2 \cos 2\theta)$$

with  $\gamma$  representing the angle between the axes  $z^{C}$  and  $z^{M}$ .

For furan- $(argon)_2$ , the vibrationally averaged inertia tensor is derived in an analogous way. Owing to the symmetry related positions of the two argon atoms, the principal axis systems of the monomer and of the complex are parallel to each other and no diagonalization is required to give

$$I_{xx}^{C} = \langle I_{xx}^{M} \rangle + 2mR^{2}\cos^{2}\theta$$

$$I_{yy}^{C} = \langle I_{yy}^{M} \rangle + Mx_{s}^{2} + 2m[(R\sin\theta - x_{s})^{2} + R^{2}\cos^{2}\theta]$$

$$I_{zz}^{C} = \langle I_{zz}^{M} \rangle + Mx_{s}^{2} + 2m(R\sin\theta - x_{s})^{2}$$
(5)

with

$$x_s = \frac{2m}{2m+M} R \sin \theta$$

The moments of inertia of the furan-(argon)<sub>n</sub>, n = 1, 2, complexes are expressed as functions of the structural parameters R and  $\theta$  and the average bending angle  $\langle \alpha \rangle$  in Eqs. (2)-(5) using the moments of inertia of the furan monomer. The three parameters  $R, \theta$ , and  $\langle \alpha \rangle$  were adjusted in an iterative least-squares fit to the observed moments of inertia of the complex. The results

Table 12 Comparison of intermolecular structures of aromatic molecule– $(\operatorname{argon})_n$ , n = 1, 2, complexes<sup>a</sup>

	R'	θ'	R⊥
Furan–Ar	3.539	9.7	3.489
Pyridine-Ar	3.545	3.2	3.539
Pyrrole-Ar	3.554	5.5	3.538
Fluorobenzene-Ar	3.584	4.8	3.572
1,2-Difluorobenzene-Ar	3.583	8.4	3.545
Furan-Ar <sub>2</sub>	3.537	10.1	3.482
Pyridine-Ar <sub>2</sub>	3.544	3.9	3.535

<sup>a</sup> Mean values of intermolecular structural parameters for all measured isotopomers calculated with Eqs. (4)–(6) from the combined results of the complexes in Refs. [2–4,17,28,29], of the aromatic monomers in Refs. [30–36] and of this work. Distances are given in Ångströms angles in degrees.

for each isotopomer with  $C_{2v}$  symmetry of furan are given in Table 10. They cannot be compared directly because R and  $\theta$  refer to the principal axis system of the individual isotopomer that experiences small shifts because of the different mass distribution. The center-of-mass of an isotopomer with  $C_{2v}$  symmetry is shifted with respect to the parent species by

$$\Delta x = \frac{1}{M} \sum_{i} (m'_i - m_i) x_i^{\mathsf{M}} \tag{6}$$

where  $m'_i - m_i$  refers to the mass difference of the isotopically substituted nucleus and the summation *i* goes over all substituted nuclei. The reduced coordinates R' and  $\theta'$  listed in Table 11 for which this shift was compensated refer to the principal axis system of the parent species.

#### 5. Discussion

The previous investigation of the furan– $(argon)_2$ complex considered only a single isotopomer, the parent species [16]. The sign of the angle  $\theta$  could not be determined from just one isotopomer. It was then assumed from analogy with the furan–argon complex. The results of the present study now prove unambiguously that the earlier assumption was justified. The two argon atoms are located perpendicularly above the ring plane on both sides of the ring as shown in Fig. 2. They are shifted towards the oxygen with respect to the center-of-mass of furan similarly to furan–argon as demonstrated from the results in Table 11.

Structure determinations of van der Waals complexes are severely affected by the large-amplitude intermolecular vibrations. In order to compensate partially for the zero-point vibrational contributions, an approximate model was developed for the bending motion of argon above the ring plane of an aromatic molecule [17]. A similar model was originally proposed by Klots et al. [4] for pyridinerare gas complexes. Our model was further extended to also include the complexes with two symmetrically located rare gas atoms above and below an aromatic ring. We tested our model rigorously with the data from a study of several isotopomers of the pyridine- $(argon)_n$ , n = 1, 2,complexes [17]. It was found there that the structure was fairly consistent and exhibited negligible variations among the isotopomers. The distances R' differed by much less than 0.005 Å and the angles  $\theta'$  by less than 1°.

Table 13

Comparison of deuterium quadrupole coupling constants (MHz) of aromatic molecules and complexes in the bond axis system<sup>a</sup>

Molecule	X22	$\chi_{xx}$	$\chi_{yy}$	$\eta^{b}$	Ref.	
Furan-3-d-Ar	0.182(5)	-0.095(5)	-0.087(6)	-0.044	This work	
Pyridine-4-d	0.196(4)	-0.090(8)	-0.106(8)	0.082	[37]	
Pyridine-4-d-Ar	0.189(4)	-0.078(4)	-0.111(4)	0.175	[4]	
Fluorobenzene-2-d	0.1876(48)	-0.0899(47)	-0.0977(22)	0.042	[38]	
Fluorobenzene-3-d	0.1909(61)	0.0879(63)	-0.1030(26)	0.079	[38]	
Fluorobenzene-4-d	0.1877(15)	-0.0890(30)	-0.0987(25)	0.054	[38]	
Benzene-d	0.1861(18)	-0.0972(23)	-0.0889(23)	-0.045	[38]	

<sup>a</sup> z refers to the C–D bond axis and y to the axis perpendicular to the ring plane.

<sup>b</sup> Asymmetry parameter  $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$ .

The present study of the structure of the furan-(argon)<sub>n</sub>, n = 1, 2, complexes confirms the consistency of the method for another series of analogous complexes. Inspection of Table 11 shows similar variations of R' and  $\theta'$  as for pyridine-(argon)<sub>n</sub>, n = 1, 2, complexes. The distances R' of the latter are marginally larger by 0.007 Å than those of the corresponding furan complexes as shown for comparison in Table 12. The angles  $\theta'$  are noticeably different. They increase by 6.3° from pyridine to furan complexes. This fact reflects itself in the shorter distances  $R_{\perp}$  of argon perpendicular above the ring plane in furan compared with pyridine.

The average bending angle  $\langle \alpha \rangle$  range is 7.7–8.6° for the isotopic complexes with one argon atom and  $10.0-10.3^{\circ}$  with two argon atoms. The variations among the isotopomers are fairly small. It is difficult to interpret the variations because the inertial axes a, b, and c change irregularly between different isotopomers. Nevertheless, the value for the furan- $d_4$ -argon complex shows the expected decrease owing to the heavier masses. The average bending angles  $\langle \alpha \rangle$  are somewhat larger for the complexes containing furan than for those containing pyridine. For complexes with one argon atom, the increase amounts to  $1^{\circ}$  whereas it rises to  $3.6^{\circ}$ for complexes with two argon atoms. Apart from these small differences, however, the structure and bending motions are remarkably similar for the observed furan- and pyridine- $(argon)_n$ , n = 1, 2, complexes.

The deuterium quadrupole splittings of the rotational transitions of furan-3-d-argon were sufficiently resolved so that it was possible to fit the quadrupole coupling constants. The diagonal coupling constants in the principal axis system were transformed to the bond axis system using the structure of the furan-argon complex in Table 12 and of the furan monomer [27]. The resulting quadrupole coupling constants  $\chi_{xx}, \chi_{yy}$ , and  $\chi_{zz}$  are given in Table 13. The z axis is defined along the C–D bond and the y axis is perpendicular to the ring plane of the aromatic monomer. The coupling constants in the bond axis system are compared to other deuterium coupling constants of aromatic molecules or complexes in Table 13. The coupling constants  $\chi_{zz}$  are grouped in a narrow range for all available examples. The asymmetry parameters  $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$  are small and only marginally significant in view of the standard deviations of the coupling constants. Their signs vary seemingly unpredictably.

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