Rotational Zeeman-Effect of [2,5-D_2]-Furan

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The high-field first and second order rotational Zeeman-effect of [2,5-D_2]-furan in the ground vibrational state has been investigated to supplement similar earlier measurements on furan [1]. The microwave spectrum [2, 3] and structure [2] of [2,5-D_2]-furan are known.

The substance was prepared according to BAK [3] et al. We employed a conventional 33.3 kHz Stark-modulated spectrometer equipped with a high-field magnet [4]. Table 1 gives the measured lines. Zeeman satellites indicated by an asterisk have been omitted in the least squares fit used for the calculation of the g-values and the susceptibility anisotropies given in Table 2. From these values together with the bulk magnetic susceptibility [5] and the structure of the nuclear frame the diagonal elements of the diamagnetic, paramagnetic and total magnetic susceptibility tensors (χ_{gg}^{d}, χ_{gg}^{p}, χ_{gg}) have been calculated ($g = a, b, c$; all tensor elements are referred to the principal axis system of the inertia tensor). From the g- and χ-tensor elements the values of the diagonal elements of the electric quadrupole tensor of the molecule, Q_{gg}, and the second moments of the electronic charge distribution, $\langle 0 | \sum_{\varepsilon} g_{\varepsilon}^2 | 0 \rangle$, have been determined. They are included in Table 2. For details see Ref. [1]. The sign of the g-values given in Table 2 is based on the value of $\langle 0 | \sum_{\varepsilon} c_{\varepsilon}^2 | 0 \rangle$, which should be positive. The set of g-values with reversed signs would result in a negative value of $\langle 0 | \sum_{\varepsilon} c_{\varepsilon}^2 | 0 \rangle$ and was therefore discarded. For comparison the corresponding values of furan are listed also in Table 2. Since in Ref. [1] $\sum Z_n a_n^2$ was errone-

Table 1. Observed Zeeman spectrum of [2,5-D_2]-furan. Those lines marked by an asterisk were not used in the least square fit.

Rotational Transition, Magnetic Field Strength [kG]	Zero Field Frequency [MHz]	Magnetic Quantum Numbers	Rel. Int.	Zeeman-Shifts $\Delta\nu_{exp}$ [MHz]	Zeeman-Shifts $\Delta\nu_{CAL}$ [MHz]	Weighted Mean Frequency [MHz]	$\Delta\nu_{exp}-\Delta\nu_{CAL}$ [kHz]
$0_{00} \rightarrow 1_{11}$	13 319.470						
$H = 24.38$		$0 \rightarrow -1$	2	− .165	− .173		8
		$0 \rightarrow 1$	2	.613	.604		9
$H = 24.09$		$0 \rightarrow 0$	1	− .422	− .422		− 1
$2_{02} \rightarrow 2_{11}$	11 756.239						
$H = 24.08$		$-2 \rightarrow -2$	4	− 3.146	− 3.106		−40
		$-1 \rightarrow -1$	1	− .721	− .735		14
		$1 \rightarrow 1$	1	—	1.553		—
		$2 \rightarrow 2$	4	1.488	1.469		19
$2_{12} \rightarrow 2_{21}$	14 243.185						
$H = 22.49$		$-1 \rightarrow -2$	4	− 2.197	− 2.236		39
		$-2 \rightarrow -1$	4	− 1.575	− 1.586		11
		$0 \rightarrow -1$	6	− .540	− .537		− 3
		$-1 \rightarrow 0$	6	.532*	.375	.435	97
		$1 \rightarrow 0$	6		.495		
		$2 \rightarrow 1$	4	.832*	.859		−27
		$0 \rightarrow 1$	6	1.703	1.669		34
		$1 \rightarrow 2$	4	2.288	2.296		− 8
$H = 24.08$		$-2 \rightarrow -2$	4	− 3.286	− 3.255		−31
		$-1 \rightarrow -1$	1	− .876	− .863		−13
		$1 \rightarrow 1$	1	—	1.627		—
		$2 \rightarrow 2$	4	1.700	1.726		−26
$1_{11} \rightarrow 2_{20}$	38 395.125						
$H = 22.48$		$-1 \rightarrow -2$	12	− 3.112	− 3.128		16
		$0 \rightarrow -1$	6	− .891	− .834		15
		$1 \rightarrow 0$	2	− .058	− .091		33
		$-1 \rightarrow 0$	2	.643	.626		17
		$1 \rightarrow 2$	12	1.880	1.859		21
		$0 \rightarrow 1$	6	2.007	2.019		−12
$H = 24.10$		$-1 \rightarrow -1$	3	− 1.088	− 1.096		8
		$0 \rightarrow 0$	4	.908	.940		−32
		$1 \rightarrow 1$	3	1.158	1.193		−35

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$1_{11} \rightarrow 2_{02}$	20 886.811						
$H = 23.70$		$1 \rightarrow 0$	2	− 1.072	− 1.083		11
		$-1 \rightarrow 0$	2	− .328	− .327		− 1
		$1 \rightarrow 2$	12	− .184	− .202		18
		$0 \rightarrow 1$	6	.116	.096		20
		$0 \rightarrow -1$	6	.236	.218		18
		$-1 \rightarrow -2$	12	.824	.798		26
$H = 25.23$		$1 \rightarrow 1$	3	− .987	− .982		− 4
		$0 \rightarrow 0$	4	− .092*	− .106	− .081	−11
		$-1 \rightarrow -1$	3		− .047		
$1_{01} \rightarrow 2_{12}$	21 891.152						
$H = 22.42$		$1 \rightarrow 0$	2	− .850	− .867		17
		$-1 \rightarrow 0$	2	− .300	− .337		37
		$1 \rightarrow 2$	2	− .013*	− .064	− .049	36
		$0 \rightarrow 1$	6		− .009		
		$0 \rightarrow -1$	6	.100	.110		−10
		$-1 \rightarrow -2$	12	.735	.705		30
$H = 25.28$		$1 \rightarrow 1$	3	− .833	− .839		6
		$0 \rightarrow 0$	4	− .220	− .229		9
		$-1 \rightarrow -1$	3	− .103	− .106		4
$1_{10} \rightarrow 2_{21}$	31 386.561						
$H = 22.40$		$0 \rightarrow -1$	6	− 1.674	− 1.643		−31
		$1 \rightarrow 0$	2	− .915	− .900		−15
		$-1 \rightarrow -2$	12	− .672	− .652		−20
		$0 \rightarrow 1$	6	.550	.554		− 4
		$1 \rightarrow 2$	12	.892	.896		− 4
		$-1 \rightarrow 0$	2	1.936	1.946		−10
$H = 24.10$		$0 \rightarrow 0$	4	− .478	− .515		37
		$1 \rightarrow 1$	3	.114	.141		26
		$-1 \rightarrow -1$	3	.819	8.39		20
$3_{03} \rightarrow 3_{12}$	21 006.938						
$H = 22.47$		$-3 \rightarrow -2$	6	− 2.795	− 2.782		−13
		$-2 \rightarrow -3$	6	− 2.610	− 2.588		−22
		$-2 \rightarrow -1$	10	− 1.207*	− 1.157	− 1.188	−19
		$-1 \rightarrow -2$	10		− 1.218		
		$0 \rightarrow -1$	12	− .138	− .130		− 8
		$-1 \rightarrow 0$	12	.173	.186		−13
		$1 \rightarrow 0$	12	.667	.676		− 9
		$0 \rightarrow 1$	12	1.208*	1.245	1.224	−16
		$2 \rightarrow 1$	10		1.199		
		$3 \rightarrow 2$	6	1.403	1.439		−36
		$1 \rightarrow 2$	10	2.001	2.023		−22
		$2 \rightarrow 3$	6	2.496	2.518		−22
$2_{21} \rightarrow 3_{12}$	36 700.796						
$H = 24.10$		$2 \rightarrow 2$	5	− .574*	− .656	− .582	12
		$1 \rightarrow 1$	8		− .536		
		$0 \rightarrow 0$	9	− .198	− .200		2
		$-1 \rightarrow -1$	8	.361	.352		9
		$-2 \rightarrow -2$	5	1.140	1.121		19

ously taken as (30.20 ± 0.04) Å² instead of (31.31 ± 0.01) Å², the values which depend on the molecular structure have been appropriately corrected.

Within the experimental uncertainties the magnetic susceptibilities of both furan and [2,5-D_2]-furan are equal as may be predicted by theory [6].

From the differences between g_{xx}^{H} and g_{xx}^{D} and between g_{zz}^{H} and g_{zz}^{D} it is in principle possible to determine the sign of the electric dipole moment [7, 8] according to the following expression:

$$\frac{g_{xx}^{D}}{G_{xx}^{D}} - \frac{g_{xx}^{H}}{G_{xx}^{H}} = -\frac{8\pi M_p}{\hbar\,|e|}\,(Y\mu_y + Z\mu_z) \quad \text{(and cycl.)}. \quad (1)$$

For the present work the z-axis has been chosen perpendicular to the plane of the ring, while the y-axis coincides with the C_2-axis of the molecule. Y and Z are the shifts of the center of mass due to the deutera-

Table 2. g-values, susceptibilities in 10^{-6} erg/G^2 Mol, structure sums in Å^2, molecular quadrupole moment in 10^{-26} esu cm^2, second moment of the charge distribution in Å^2. — The calculated quantities marked by an asterisk differ from those obtained by SUTTER [1] et al., who erroneously used a value of $\sum Z_n a_n^2 = 30.20 \pm 0.04$ Å^2. For the two isotopic species the a- and b-axis have changed under deuteration. The uncertainties of the g-values and susceptibility anisotropies are the standard deviations.

Furan	[2,5-D_2]-furan
$g_{aa} = -0.0911 \pm 0.0007$	$g_{bb} = -0.07793 \pm 0.0004$
$g_{bb} = -0.0913 \pm 0.0002$	$g_{aa} = -0.08875 \pm 0.00034$
$g_{cc} = +0.0511 \pm 0.0001$	$g_{cc} = +0.04692 \pm 0.00029$
$\sum Z_n a_n^2 = 31.31 \pm 0.01$*	$\sum Z_n b_n^2 = 31.38 \pm 0.01$
$\sum Z_n b_n^2 = 32.62 \pm 0.03$	$\sum Z_n a_n^2 = 32.61 \pm 0.03$
$\sum Z_n c_n^2 = 0$	$\sum Z_n c_n^2 = 0$
$2\chi_{aa} - \chi_{bb} - \chi_{cc} = 43.0 \pm 0.2$	$2\chi_{bb} - \chi_{aa} - \chi_{cc} = 43.4 \pm 0.5$
$2\chi_{bb} - \chi_{aa} - \chi_{cc} = 34.4 \pm 0.2$	$2\chi_{aa} - \chi_{bb} - \chi_{cc} = 33.5 \pm 0.6$
$\frac{1}{3}(\chi_{aa} + \chi_{bb} + \chi_{cc}) = -44.8 \pm 1.5$	$\frac{1}{3}(\chi_{aa} + \chi_{bb} + \chi_{cc}) = -44.8 \pm 1.5$
$\chi^d_{aa} = -189.4 \pm 1.9$	$\chi^d_{bb} = -189.1 \pm 1.8$
$\chi^d_{bb} = -187.2 \pm 1.7$*	$\chi^d_{aa} = -187.7 \pm 1.9$
$\chi^d_{cc} = -318.6 \pm 1.7$*	$\chi^d_{cc} = -318.7 \pm 2.0$
$\chi^p_{aa} = 158.9 \pm 0.3$	$\chi^p_{bb} = 158.7 \pm 0.2$
$\chi^p_{bb} = 153.9 \pm 0.1$*	$\chi^p_{aa} = 154.1 \pm 0.1$
$\chi^p_{cc} = 248.0 \pm 0.1$*	$\chi^p_{cc} = 248.3 \pm 0.3$
$\chi_{aa} = -30.4 \pm 1.6$	$\chi_{bb} = -30.3 \pm 1.7$
$\chi_{bb} = -33.3 \pm 1.6$	$\chi_{aa} = -33.6 \pm 1.7$
$\chi_{cc} = -70.6 \pm 1.6$	$\chi_{cc} = -70.4 \pm 1.9$
$Q_{aa} = 0.2 \pm 0.4$	$Q_{bb} = -0.2 \pm 0.5$
$Q_{bb} = 5.9 \pm 0.3$	$Q_{aa} = 6.4 \pm 0.6$
$Q_{cc} = -6.1 \pm 0.4$	$Q_{cc} = -6.2 \pm 0.9$
$\langle a^2 \rangle = 37.28 \pm 0.6$*	$\langle b^2 \rangle = 37.39 \pm 0.7$
$\langle b^2 \rangle = 37.80 \pm 0.6$	$\langle a^2 \rangle = 37.70 \pm 0.7$
$\langle c^2 \rangle = 6.84 \pm 0.6$	$\langle c^2 \rangle = 6.85 \pm 0.7$

tion, referred to the principal axis system of the parent molecule. (The positive y-axis points from the 0-nucleus towards the center of the molecule: $Y = -0.023_3$ Å; $Z = 0$.) G_{gg} are the rotational constants. For the non-deuterated species the values determined by BAK and coworkers [2] have been used, i. e. $G_{xx}^H = B^H = 9246.61$, $G_{yy}^H = A^H = 9446.96$, and $G_{zz}^H = C^H = 4670.88$ (all values in MHz). The rotational constants for the deuterated species have been redetermined, using the zero-field transition frequencies given in Table 1. In view of the fact that only transitions with low J values have been measured the rigid rotor approximation has been used for the least squares fit. The following values have been obtained:

$$G_{xx}^D = A^D = 9033.58_4 \pm 0.014\,,$$
$$G_{yy}^D = B^D = 8160.74_8 \pm 0.011\,,$$
and $$G_{zz}^D = C^D = 4285.85_4 \pm 0.010 \text{ MHz}$$

(the uncertainties given are twice the standard deviations). Although the differences in the g-values are comparatively large for the two isotopic species so far measured, it is not possible to determine the sign of the electric dipole moment conclusively [$|\mu| = (0.661 \pm 0.006)$ D from Stark effect measurements [9]], since the change in the g-values is largely compensated by the change in the rotational constants. If one inserts the appropriate values into Eq. (1) one arrives at $\mu_y = +(2.6 \pm 2.3)$ D (using the equation involving g_{xx}), and $\mu_y = +(0.5 \pm 3.6)$ D (using the equation involving g_{zz}). This result may indicate that the negative charge associated with the electric dipole moment is at the oxygen side of the molecule. Recently, by an ab initio procedure, PALMER and GASKELL [10] calculated $\mu = 0.64$ D (negative end at oxygen).

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