^{14}N Quadrupole Coupling in the Rotational Spectrum of Nitrosobenzene

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As the technique of microwave Fourier transform (MWFT) spectroscopy was improved in the recent years we give a reinvestigation of the ^{14}N nuclear quadrupole hyperfine structure of nitrosobenzene.

We present a refined measurement and analysis of the ^{14}N quadrupole hyperfine coupling in the rotational spectrum of nitrosobenzene, C_6H_5NO, which was investigated by microwave Fourier transform (MWFT) spectroscopy in 1981 in the range from 8 to 12 GHz [1]. We remeasured the lines in this region and recorded some more transitions in the J- and Ku-band. As can be seen from a comparison of Fig. 1 with Fig. 1 of [1] the technique was improved.

The substance was purchased from Fa. Aldrich, Steinheim, with a purity of 97% and used without further purification. The spectra were taken with our MWFT-spectrometers [2–4] in the range from 5 to 18 GHz at pressures between 0.025 and 0.13 Pa (0.2 to 1 mTorr) and a temperature of − 50 °C. To avoid overlapping effects in the multiplets the time domain signals were analysed by a computer program [5, 6] to obtain the frequencies, amplitudes, phases and line widths contained in the signals. The measurements are given in Table 1. The assignment was checked by a fourth order centrifugal distortion analysis applied to the lines of Table 1 using Watsons *S*-reduction [7]. A first order hfs analysis was carried out [8], which was checked by a program using direct diagonalisation [9].

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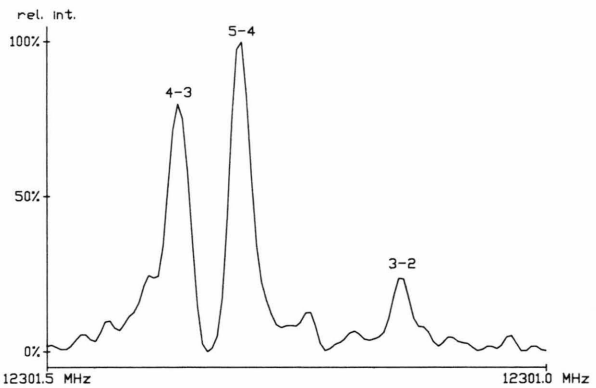

Fig. 1. Nitrogen hfs of the transition $4_{13} - 3_{12}$, power spectrum, polarisation frequency: 12 300 MHz, sample interval 50 ns, $14.5 \cdot 10^6$ averaging cycles, 1024 data points supplemented with 3096 zeros, pressure: 0.5 mT, temperature: − 50 °C.

Table 1. Measured line frequencies of nitrosobenzene with hfs-splittings. ν: measured frequency, $\Delta\nu_{hfs}$: hfs-splitting referred to the strongest component, δ_{hfs}: deviation of the experimental and the calculated splitting, ν_0: hypothetical unsplit line frequency calculated by adding the hfs-splittings to the frequencies of the components, δ_0: deviation of the centrifugal distortion calculation.

J	K_-	K_+	$-J'$	K'_-	K'_+	$F - F'$	ν [MHz]	$\Delta\nu_{hfs}$ [MHz]	δ_{hfs} [KHz]	ν_0 [MHz]	δ_0 [KHz]
2	1	1	− 1	1	0	3 − 2	6181.681			6 181.791	0
						2 − 1	6 181.806	−0.125	5		
3	0	3	− 2	0	2	4 − 3	8 566.389			8 566.321	−1
						3 − 2	8 566.135	0.255	1		
						2 − 1	8 566.446	−0.057	−1		

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Table 1 (continued)

J	K_-	$K_+ - J'$	K'_-	K'_+	$F - F'$	ν [MHz]	$\Delta\nu_{hfs}$ [MHz]	δ_{hfs} [KHz]	ν_0 [MHz]	δ_0 [KHz]
4	2	2 – 3	2	1	5 – 4	11 848.618			11 848.703	0
					4 – 3	11 848.911	−0.293	1		
					3 – 2	11 848.572	0.047	−11		
4	0	4 – 3	0	3	5 – 4	11 289.804			11 289.710	−3
					4 – 3	11 289.476	0.328	0		
					3 – 2	11 289.846	−0.042	−4		
4	3	1 – 3	3	0	5 – 4	11 645.804			11 645.834	2
					3 – 2					
					4 – 3	11 645.911	−0.108	5		
4	1	3 – 3	1	2	5 – 4	12 298.686			12 298.698	−2
					4 – 3	12 298.632	0.053	2		
					3 – 2	12 298.850	−0.164	1		
4	3	2 – 3	3	1	5 – 4	11 637.102			11 637.132	−4
					3 – 2					
					4 – 3	11 637.192	−0.090	1		
5	0	5 – 4	0	4	6 – 5	13 920.805			13 920.696	0
					5 – 4	13 920.445	0.360	4		
					4 – 3	13 920.843	−0.038	3		
5	1	4 – 4	1	3	6 – 5	15 306.719			15 306.706	−2
					5 – 4	15 306.610	0.109	−1		
					4 – 3	15 306.825	−0.106	1		
5	1	5 – 4	1	4	6 – 5	13 380.515			13 380.463	1
					5 – 4	13 380.393	0.122	−7		
					4 – 3	13 380.429	0.086	−12		
6	0	6 – 5	0	5	7 – 6	16 469.763			16 469.653	−1
					6 – 5	16 469.410	0.353	−4		
					5 – 4	16 469.795	−0.032	6		
6	1	6 – 5	1	5	7 – 6	15 994.045			15 993.996	1
					6 – 5	15 993.935	0.110	8		
					5 – 4	15 994.011	0.034	14		
10	2	8 – 10	2	9	11 – 11	9 511.430			9 512.128	−2
					10 – 10	9 513.731	−2.103	−2		
					9 – 9	9 511.196	0.234	−3		
11	2	9 – 11	2	10	12 – 12	12 332.614			12 333.333	−3
					11 – 11	12 334.967	−2.352	0		
					10 – 10	12 332.396	0.218	−3		
14	3	11 – 14	3	12	15 – 15	9 967.041			9 967.595	3
					14 – 14	9 968.826	−1.785	4		
					13 – 13	9 966.913	0.128	−1		
18	4	14 – 18	4	15	19 – 19	9 739.825			9 740.277	0
					18 – 18	9 741.250	−1.425	−5		
					17 – 17	9 739.743	0.082	−3		
22	5	17 – 22	5	18	23 – 23	9 047.087			9 047.456	1
					22 – 22	9 048.244	−1.156	0		
					21 – 21	9 047.035	0.053	1		
23	5	18 – 23	5	19	24 – 24	12 121.523			12 121.940	0
					23 – 23	12 122.827	−1.304	−2		
					22 – 22	12 121.464	0.059	−2		
27	6	21 – 27	6	22	28 – 28	11 012.836			11 013.184	−1
					27 – 27	11 013.918	−1.082	−2		
					26 – 26	11 012.794	0.042	−3		
31	7	24 – 31	7	25	32 – 32	9 683.058			9 683.358	1
					30 – 30					
					31 – 31	9 683.957	−0.899	−4		
35	8	27 – 35	8	28	36 – 36	8 277.777			8 278.017	0
					34 – 34					
					35 – 35	8 278.500	−0.723	−5		

Table 2. Rotational, centrifugal distortion, and quadrupole coupling constants of nitrosobenzene, A, B, C: rotational constants, D_J, D_{JK} D_K, d_1, d_2: fourth order centrifugal distortion constants according to Watsons S-reduction, æ: asymmetry parameter, χ^+, χ^-: quadrupole coupling constants, $\Delta\bar{\nu}_{exp}$: mean experimental hfs-splitting, σ: standard deviation of the fit, standard errors in brackets, $|(\chi^+, \chi^-)|$: correlation coefficient.

A	5249.143	(74) MHz						
B	1643.273	(4) MHz						
C	1251.976	(3) MHz						
D_J	0.0556	(59) kHz						
D_{JK}	0.207	(36) kHz						
D_K	1.71	(41) kHz						
d_1	−0.0161	(9) kHz						
d_2	−0.00675	(93) kHz						
æ	−0.8042							
σ	0.003	MHz						
Correlation matrix								
A	1.000							
B	0.390	1.000						
C	−0.274	0.726	1.000					
D_J	0.281	0.906	0.785	1.000				
D_{JK}	−0.125	0.538	0.459	0.350	1.000			
D_K	−0.752	−0.645	−0.062	−0.448	−0.539	1.000		
d_1	−0.828	−0.595	0.089	−0.392	−0.332	0.905	1.000	
d_2	0.972	0.397	−0.285	0.275	−0.083	−0.769	−0.899	1.000
$\chi^+ = \chi_{bb} + \chi_{cc}$	−0.042	(8) MHz						
$\chi^- = \chi_{bb} - \chi_{cc}$	−10.013	(10) MHz						
χ_{aa}	0.042	(8) MHz						
χ_{bb}	−5.028	(9) MHz						
χ_{cc}	4.986	(9) MHz						
$\|(\chi^+, \chi^-)\|$	−0.109							
$\Delta\bar{\nu}_{exp}$	0.462	MHz						
σ	0.005	MHz						

A mean splitting of 462 kHz was fitted with a standard deviation of 5 kHz. Both the results of the centrifugal distortion and the hfs analysis are presented in Table 2. The standard deviation of the coupling constants could be reduced by a factor of six.

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