

Quadrupole Hyperfine Structure in the Rotational Spectrum of Benzonitrile

K. Vormann, U. Andresen, N. Heineking, and H. Dreizler

Abteilung Chemische Physik
im Institut für Physikalische Chemie der Universität Kiel

Z. Naturforsch. **43a**, 283–284 (1988);
received December 11, 1987

We reinvestigated the quadrupole coupling of benzonitrile by an improved technique of microwave Fourier transform (MWFT) spectroscopy and evaluation method. The error of the coupling constants was reduced by one order of magnitude.

One of the first molecules we investigated by MWFT spectroscopy was benzonitrile, C_6H_5CN [1]. Benzonitrile is a reference molecule for the investigation of effects caused by substitution [2]. Meanwhile the technique of MWFT spectroscopy [3, 4] was improved and the frequency range was extended. We further noticed that the spectra have to be evaluated more elaborately [5–8]. In Fig. 1 we show a recording of the same transition as presented in Fig. 1 of [1]. The improvement is clearly visible. The substance, 99% pure, was purchased from Merck, Darmstadt. The spectra were recorded at temperatures between -30° to $-50^\circ C$ and pressures between 0.1 and 1 mTorr (0.013–0.13 Pa). In Table 1 we give the frequencies of the new measurements. A detailed study of the centrifugal distortion was not intended. Therefore we report in Table 2 only the rotational constants resulting from a calculation with Watson's A reduction [9]. Lines of Table 2 of [10] were included. Because the precision of

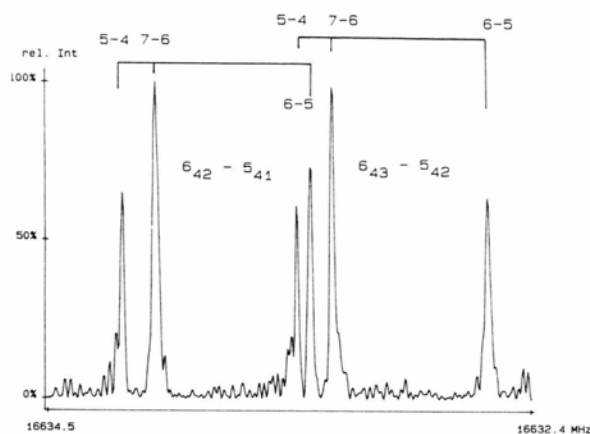


Fig. 1. Nitrogen-hfs of the K-doublet $6_{42} - 5_{41}$, $6_{43} - 5_{42}$. The F quantum numbers are given in addition. Polarizing frequency 16632.3 MHz. Sample interval 50 ns, 1024 sampling points. Zero filling to 4096 points prior to Fourier transformation, spectral point distance 5 kHz, $1.3 \cdot 10^7$ averaging cycles, measuring time 15 min. Temperature $-50^\circ C$, pressure 0.1 mTorr.

the MWFT and Stark spectrometer measurements are different, the deviations δ_0 of Table 1 are relatively large. The hfs was analysed by first order theory [11], which has been proved to be sufficient [1]. The quadrupole coupling constants are listed in Table 2. A comparison with Table 1 of [1] shows, that the standard errors of the χ^+ and χ^- are reduced by more than one order of magnitude.

We thank the members of our group for help and discussion, the Deutsche Forschungsgemeinschaft, the Land Schleswig-Holstein and the Fonds der Chemie for funds. The calculations were made at the computer center of the university.

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Reprint requests to Prof. Dr. H. Dreizler, Institut für Physikalische Chemie der Universität Kiel, Olshausenstr. 40–60, D-2300 Kiel.

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Table 1. Measured line frequencies [MHz] of benzonitrile with hfs-splittings. ν : measured frequency, $\Delta\nu_{\text{hfs}}$: hfs-splitting referred to the strongest component, δ_{hfs} : deviation of the experimental and the calculated splitting, ν_0 : hypothetical unsplit line frequency calculated with the hfs-splittings added to the frequencies of the components, δ_0 [kHz]: deviation from the centrifugal distortion calculation

J	K_-	$K_+ - J'$	K'_-	K'_+	$F - F'$	ν [MHz]	$\Delta\nu_{\text{hfs}}$ [MHz]	δ_{hfs} [MHz]	ν_0 [MHz]	δ_0 [kHz]
5	4	1 -	4	4	0	6 - 5	13 849.721		13 849.425	23
						5 - 4	13 848.573	1.148 -0.001		
						4 - 3	13 850.061	-0.340 -0.002		
5	2	3 -	4	2	2	6 - 5	14 132.251		14 132.156	5
						5 - 4	14 131.935	0.316 0.001		
						4 - 3	14 132.283	-0.032 0.000		
5	0	5 -	4	0	4	6 - 5	13 437.373		13 437.359	-1
						5 - 4	13 437.373			
						4 - 3	13 437.302	0.072 0.000		
5	3	2 -	4	3	1	6 - 5	13 880.677		13 880.500	12
						5 - 4	13 880.020	0.657 0.000		
						4 - 3	13 880.838	-0.161 0.001		
5	1	4 -	4	1	3	6 - 5	14 545.180		14 545.141	7
						5 - 4	14 545.094	0.086 0.002		
						4 - 3	14 545.128	0.051 -0.001		
5	1	5 -	4	1	4	6 - 5	12 897.587		12 897.550	-5
						5 - 4	12 897.499	0.088 -0.001		
						4 - 3	12 897.543	0.044 0.001		
5	4	2 -	4	4	1	6 - 5	13 849.561		13 849.265	12
						5 - 4	13 848.415	1.146 0.001		
						4 - 3	13 849.900	-0.339 -0.003		
6	4	2 -	5	4	1	7 - 6	16 634.031		16 633.846	24
						6 - 5	16 633.357	0.674 -0.002		
						5 - 4	16 634.173	-0.142 -0.002		
6	5	1 -	5	5	0	7 - 6	16 616.134		16 615.855	39
						6 - 5	16 615.097	1.037 0.002		
						5 - 4	16 616.389	-0.255 0.003		
6	4	3 -	5	4	2	7 - 6	16 633.267		16 633.082	21
						6 - 5	16 632.591	0.676 -0.004		
						5 - 4	16 633.412	-0.145 0.001		
9	2	7 -	9	2	8	10 - 10	5 049.222		5 049.187	14
						8 - 8				
						9 - 9	5 049.113	0.109 0.001		
13	2	11 -	13	2	12	14 - 14	14 717.024		14 716.988	57
						12 - 12				
						13 - 13	14 716.912	0.111 0.002		
17	3	14 -	17	3	15	18 - 18	13 684.760		13 684.724	30
						16 - 16				
						17 - 17	13 684.651	0.109 0.001		
18	3	15 -	18	3	16	19 - 19	16 845.710		16 845.669	41
						17 - 17				
						18 - 18	16 845.596	0.114 -0.004		
22	4	18 -	22	4	19	23 - 23	14 814.832		14 814.798	19
						21 - 21				
						22 - 22	14 814.725	0.106 -0.005		
27	5	22 -	27	5	23	28 - 28	15 398.467		15 398.436	20
						26 - 26				
						27 - 27	15 398.378	0.089 0.004		

Table 2. Rotational [MHz] and quadrupole coupling constants [MHz] of benzonitrile. $|(\chi^+, \chi^-)|$ correlation coefficient. Standard deviation of the hfs analysis of 25 splittings is 2 kHz, mean splitting is 322 kHz.

A	5655.314 (16)
B	1546.8768 (15)
C	1214.4032 (14)
χ^+	4.244 (4)
χ^-	0.336 (5)
$ (\chi^+, \chi^-) $	-0.07
χ_{aa}	-4.244 (4)
χ_{bb}	2.290 (5)
χ_{cc}	1.954 (5)