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

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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 $-50°C$ 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 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.

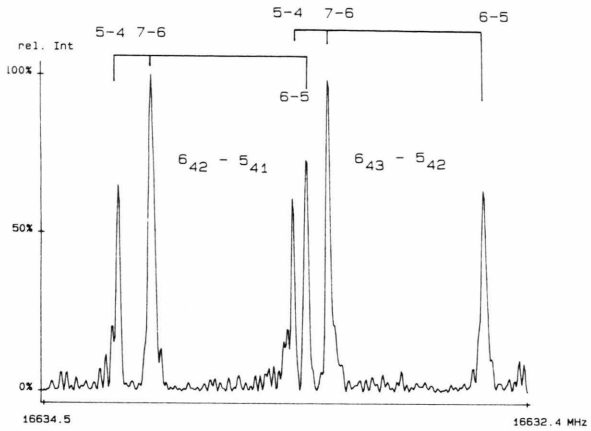

Fig. 1. Nitrogen-hfs of the K-doublet $6_{42} - 5_{41}$, $6_{43} - 5_{42}$. The F quantum numbers are given in addition. Polarizing frequency 16 632.3 MHz. Sample interval 50 ns, 1024 sampling points. Zero filling to 4096 points prior to Fourier transformation, spectral point distance 5 kHz, $1.3 \cdot 10^7$ averaging cycles, measuring time 15 min. Temperature $-50°C$, pressure 0.1 mTorr.

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[1] E. Fliege, G. Bestmann, R. Schwarz, and H. Dreizler, Z. Naturforsch **36a**, 1124 (1981).
[2] O. Böttcher and D. Sutter, Z. Naturforsch. **43a**, 47 (1988).
[3] H. Dreizler, Molecular Physics, **59**, No. 1, 1–28 (1986).
[4] W. Stahl, G. Bestmann, H. Dreizler, U. Andresen, and R. Schwarz, Rev. Sci. Instrum. **56**, 1759 (1985) and citations therein.
[5] E. Fliege and H. Dreizler, Z. Naturforsch. **39a**, 630 (1984).
[6] I. Merke, Diplom Thesis 1986.
[7] I. Merke and H. Dreizler, Z. Naturforsch. **43a**, 203 (1988).
[8] J. Haekel and H. Mäder, Z. Naturforsch. **43a**, 196 (1988).
[9] J. K. G. Watson in "Vibrational Spectra and Structure" (J. R. Durig Ed) Vol 6, Elsevier, New York 1977, p. 33.
[10] J. Casado, L. Nygaard, and G. O. Sørensen, J. Mol. Struct. **8**, 211 (1971).
[11] W. Gordy and R. L. Cook, Microwave Molecular Spectra, John Wiley and Sons, New York 1984, Chapter IX.

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, $\Delta\nu_{hfs}$: 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]	$\Delta\nu_{hfs}$ [MHz]	δ_{hfs} [MHz]	ν_0 [MHz]	δ_0 [kHz]
5	4	1	− 4	4	0	6 − 5	13849.721			13849.425	23
						5 − 4	13848.573	1.148	−0.001		
						4 − 3	13850.061	−0.340	−0.002		
5	2	3	− 4	2	2	6 − 5	14132.251			14132.156	5
						5 − 4	14131.935	0.316	0.001		
						4 − 3	14132.283	−0.032	0.000		
5	0	5	− 4	0	4	6 − 5					
						5 − 4	13437.373			13437.359	−1
						4 − 3	13437.302	0.072	0.000		
5	3	2	− 4	3	1	6 − 5	13880.677			13880.500	12
						5 − 4	13880.020	0.657	0.000		
						4 − 3	13880.838	−0.161	0.001		
5	1	4	− 4	1	3	6 − 5	14545.180			14545.141	7
						5 − 4	14545.094	0.086	0.002		
						4 − 3	14545.128	0.051	−0.001		
5	1	5	− 4	1	4	6 − 5	12897.587			12897.550	−5
						5 − 4	12897.499	0.088	−0.001		
						4 − 3	12897.543	0.044	0.001		
5	4	2	− 4	4	1	6 − 5	13849.561			13849.265	12
						5 − 4	13848.415	1.146	0.001		
						4 − 3	13849.900	−0.339	−0.003		
6	4	2	− 5	4	1	7 − 6	16634.031			16633.846	24
						6 − 5	16633.357	0.674	−0.002		
						5 − 4	16634.173	−0.142	−0.002		
6	5	1	− 5	5	0	7 − 6	16616.134			16615.855	39
						6 − 5	16615.097	1.037	0.002		
						5 − 4	16616.389	−0.255	0.003		
6	4	3	− 5	4	2	7 − 6	16633.267			16633.082	21
						6 − 5	16632.591	0.676	−0.004		
						5 − 4	16633.412	−0.145	0.001		
9	2	7	− 9	2	8	10 − 10					
						8 − 8	5049.222			5049.187	14
						9 − 9	5049.113	0.109	0.001		
13	2	11	− 13	2	12	14 − 14					
						12 − 12	14717.024			14716.988	57
						13 − 13	14716.912	0.111	0.002		
17	3	14	− 17	3	15	18 − 18					
						16 − 16	13684.760			13684.724	30
						17 − 17	13684.651	0.109	0.001		
18	3	15	− 18	3	16	19 − 19					
						17 − 17	16845.710			16845.669	41
						18 − 18	16845.596	0.114	−0.004		
22	4	18	− 22	4	19	23 − 23					
						21 − 21	14814.832			14814.798	19
						22 − 22	14814.725	0.106	−0.005		
27	5	22	− 27	5	23	28 − 28					
						26 − 26	15398.467			15398.436	20
						27 − 27	15398.378	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)
$\lvert(\chi^+, \chi^-)\rvert$	−0.07	
χ_{aa}	−4.244	(4)
χ_{bb}	2.290	(5)
χ_{cc}	1.954	(5)