

Quadrupole Coupling in Benzonitrile An Application of Microwave Fourier Transform Spectroscopy

E. Fliege, G. Bestmann, R. Schwarz, and H. Dreizler
Abteilung Chemische Physik im Institut für
Physikalische Chemie der Universität Kiel

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The microwave spectrum of benzonitrile, C_6H_5CN , was thoroughly investigated by several authors [1–5]. The r_s -structure, the dipole moment and centrifugal distortion constants have been determined. For the nitrogen-hfs only an estimate exists [4]. By use of Microwave Fourier transform Spectroscopy [6, 7] we were able to investigate the nitrogen-hfs. Benzonitrile 99% was purchased from Merck, Darmstadt, and used after vacuum distillation. The spectra were taken at -50 to -60 °C and pressures down to 0.3 mT.

The assignment of the measured lines was checked by a centrifugal distortion analysis [8, 9] using the intensity weighted mean of the hfs-components. 47 lines of Table 1 and Table 2 of [4] were fitted with

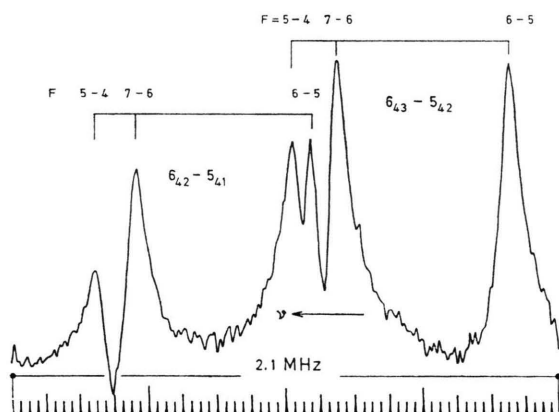


Fig. 1. Nitrogen-hfs of the K-doublet $642-541$, $643-542$ measured with MWFT spectroscopy. Transient emission recorded in steps of 50 ns for 1024 points. Measuring time 10 min. for a 10 MHz range. Zeros up to 2048 points were added prior to the Fourier transformation. Spectral points at 10 kHz distance. Frequencies calculated by three point interpolation Lorentz profile assumed. Pressure 0.1 mT, temperature -57 °C.

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

Table 1. Measured lines [MHz] of benzonitrile with hfs-splittings. The intensity weighted mean $\bar{\nu}$ was used for the centrifugal distortion analysis. $\Delta\nu_{\text{calc}}$ was calculated with the constants of Table 2. Measuring accuracy 20 kHz. Mean square deviation of the fit 39 kHz.

$J_{K-K+} - J'_{K'-K'+}$	$F - F'$	ν_{exp}	$\bar{\nu}$	$\Delta\nu_{\text{exp}}$	$\Delta\nu_{\text{calc}}$
$3_{03} - 2_{02}$	4 – 3	8206.817	8206.756	0.284	0.247
	3 – 2				
	2 – 1	8206.533			
$3_{22} - 2_{21}$	2 – 1	8284.877	8283.848	0.756	0.748
	4 – 3	8284.121			
	3 – 2	8282.757		1.364	1.346
$4_{04} - 3_{03}$	5 – 4	10855.259	10855.224	0.142	0.117
	4 – 3				
	3 – 2	10855.117			
$5_{05} - 4_{04}$	6 – 5	13437.379	13437.355	0.089	0.073
	5 – 4				
	4 – 3	13437.290			
$5_{42} - 4_{41}$	4 – 3	13850.059	13849.373	0.461	0.337
	6 – 5	13849.598			
	5 – 4	13848.541		1.057	1.132
$6_{06} - 6_{05}$	7 – 6	15951.941	15951.923	0.063	0.051
	6 – 5				
	5 – 4	15951.878			
$6_{34} - 5_{33}$	5 – 4	16655.514	16655.336	0.075	0.059
	7 – 6	16655.439			
	6 – 5	16655.063		0.376	0.381
$6_{42} - 5_{41}$	5 – 4	16634.184	16633.848	0.161	0.142
	7 – 6	16634.023			
	6 – 5	16633.358		0.665	0.663
$6_{43} - 5_{42}$	5 – 4	16633.427	16633.085	0.172	0.142
	7 – 6	16633.255			
	6 – 5	16632.595		0.660	0.663
$6_{51} - 5_{50}$	5 – 4	16616.407	16615.866	0.288	0.249
	7 – 6	16616.119			
	6 – 5	16615.109		1.010	1.025
$7_{16} - 7_{17}$	8 – 8	9163.970	9163.922	0.147	0.143
	6 – 6				
	7 – 7	9163.823			
$8_{17} - 8_{18}$	9 – 9	11654.532	11654.490	0.128	0.135
	7 – 7				
	8 – 8	11654.404			
$5_{24} - 4_{23}^a$	6 – 5	13763.406	13763.314	0.280	0.310
	4 – 3				
	5 – 4	13763.126			

^a not included in the fit.

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Table 2. Rotational [MHz] and centrifugal distortion [kHz] constants of Benzonitrile determined by centrifugal distortion analysis of 47 lines with a mean square deviation of the fit of 41 kHz. Highest correlation coefficient $|(\delta_J, \delta_K)| = 0.987$. Nitrogen quadrupole coupling constants [MHz]. Correlation coefficient 0.02. Standard errors are given.

A	5655.154 $\pm$ 0.05
B	1546.877 $\pm$ 0.001
C	1214.404 $\pm$ 0.001
κ	- 0.850263
Δ_J	0.0535 $\pm$ 0.008
Δ_{JK}	0.772 $\pm$ 0.03
Δ_K	6.1 $\pm$ 1.2
δ_J	0.0043 $\pm$ 0.002
δ_K	1.33 $\pm$ 0.2
$\chi^+ = \chi_{bb} + \chi_{cc}$	4.187 $\pm$ 0.07
$\chi^- = \chi_{bb} - \chi_{cc}$	0.416 $\pm$ 0.08
χ_{aa}	- 4.187 $\pm$ 0.16
χ_{bb}	2.301 $\pm$ 0.08
χ_{cc}	1.886 $\pm$ 0.08

a mean square deviation of 41 kHz. The highest correlation coefficient was $|(\delta_J, \delta_K)| = 0.987$. The rotational constants in Table 2 agree within the error limits with those of [4]. We take this centrifugal distortion analysis only as a kind of interpolation.

The hfs was analysed by first order perturbation theory. These calculations were checked by a program NQHFS [10] using diagonalisation of a sufficiently large submatrix of the Hamiltonian matrix. The results are given in Table 2. A mean splitting of 439 kHz was fitted with a mean square deviation of 39 kHz.

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