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

Z. Naturforsch. **36a**, 1124–1125 (1981);
received August 21, 1981

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

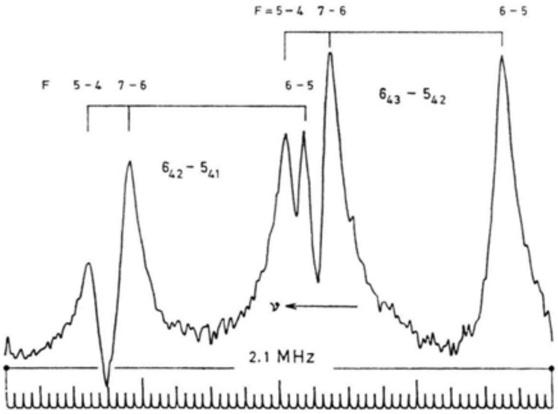

Fig. 1. Nitrogen-hfs of the K-dublett $6_{42}-5_{41}$, $6_{43}-5_{42}$ measured with MWFT spectroscopy. Transient emission recorded in steps of 50 ns for 1024 points. Measuring time 10 min. for a 10 MHz range. Zeros up to 2048 points were added prior to the Fourier transformation. Spectral points at 10 kHz distance. Frequencies calculated by three point interpolation Lorentz profile assumed. Pressure 0.1 mT, temperature −57 °C.

Table 1. Measured lines [MHz] of benzonitrile with hfs-splittings. The intensity weighted mean $\bar{\nu}$ was used for the centrifugal distortion analysis. $\Delta\nu_{calc}$ 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}	$\bar{\nu}$	$\Delta\nu_{exp}$	$\Delta\nu_{calc}$
$3_{03} - 2_{02}$	4 − 3 3 − 2 2 − 1	8206.817 8206.533	8206.756	0.284	0.247
$3_{22} - 2_{21}$	2 − 1 4 − 3 3 − 2	8284.877 8284.121 8282.757	8283.848	0.756 1.364	0.748 1.346
$4_{04} - 3_{03}$	5 − 4 4 − 3 3 − 2	10855.259 10855.117	10855.224	0.142	0.117
$5_{05} - 4_{04}$	6 − 5 5 − 4 4 − 3	13437.379 13437.290	13437.355	0.089	0.073
$5_{42} - 4_{41}$	4 − 3 6 − 5 5 − 4	13850.059 13849.598 13848.541	13849.373	0.461 1.057	0.337 1.132
$6_{06} - 6_{05}$	7 − 6 6 − 5 5 − 4	15951.941 15951.878	15951.923	0.063	0.051
$6_{34} - 5_{33}$	5 − 4 7 − 6 6 − 5	16655.514 16655.439 16655.063	16655.336	0.075 0.376	0.059 0.381
$6_{42} - 5_{41}$	5 − 4 7 − 6 6 − 5	16634.184 16634.023 16633.358	16633.848	0.161 0.665	0.142 0.663
$6_{43} - 5_{42}$	5 − 4 7 − 6 6 − 5	16633.427 16633.255 16632.595	16633.085	0.172 0.660	0.142 0.663
$6_{51} - 5_{50}$ $6_{52} - 5_{51}$	5 − 4 7 − 6 6 − 5	16616.407 16616.119 16615.109	16615.866	0.288 1.010	0.249 1.025
$7_{16} - 7_{17}$	8 − 8 6 − 6 7 − 7	9163.970 9163.823	9163.922	0.147	0.143
$8_{17} - 8_{18}$	9 − 9 7 − 7 8 − 8	11654.532 11654.404	11654.490	0.128	0.135
$5_{24} - 4_{23}$[a]	6 − 5 4 − 3 5 − 4	13763.406 13763.126	13763.314	0.280	0.310

[a] not included in the fit.

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

0340-4811 / 81 / 1000-1124 $ 01.00/0. — Please order a reprint rather than making your own copy.

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

We thank the members of our group for many discussions, Mr. R. Palm for preliminary calculations, the Deutsche Forschungsgemeinschaft and Fonds der Chemie for funds. The calculations were made with the computer of the University Computer Center.

[1] G. Erlandson, J. Chem. Phys. **22**, 1152 (1954).
[2] D. R. Lide, jr., J. Chem. Phys. **22**, 1577 (1954).
[3] G. Erlandson, Ark. Fysik **9**, 399 (1955).
[4] J. Casado, L. Nygaard, and G. O. Sørensen, J. Mol. Struct. **8**, 211 (1971).
[5] B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard, and J. Rastrup-Andersen, J. Chem. Phys. **37**, 2027 (1962).
[6] G. Bestmann, H. Dreizler, H. Mäder, and U. Andresen, Z. Naturforsch. **35a**, 392 (1980).
[7] MWFT-Spectrometer in X-Band to be published.
[8] J. K. G. Watson, J. Chem. Phys. **46**, 1935 (1967).
[9] V. Typke, Z. Naturforsch. **26a**, 1775 (1971). Programms VT 26 and VT 27.
[10] D. Hübner and M. Stolze, Diplomarbeiten Kiel 1980.