Quadrupole Coupling in Butyronitrile

An Application of Microwave Fourier Transform Spectroscopy

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The microwave spectrum of butyronitrile, $CH_3CH_2CH_2CN$, was already investigated by Hirota [1]. But he could not observe the quadrupole hyperfine structure due to the nitrogen nucleus because the lines were too broad. By use of Microwave Fourier Transform Spectroscopy [2, 3] we were able to investigate the nitrogen-hfs. The spectra were taken at −60 °C and pressures down to 0.3 mTorr. Some lines were also measured with a high resolution Stark spectrometer [4, 5] in order to compare the two methods. The results are in good agreement but it clearly appears that the Fourier Spectroscopy is far better adapted to the measurement of narrow splittings. The measured lines are reported in Table 1 for the gauche form and in Table 2 for the trans form. Figure 1 shows a typical splitting. The hyperfine structure was analyzed by first order perturbation theory using the observed rotational constants of Hirota [1] Table II. It was checked that this approximation is sufficient. The results are given in Table 3. The fitting parameters were χ^+ and χ^-. Within the measuring range there was no line sensitive to χ_{ab}. For the gauche form, a mean splitting $\overline{\Delta\nu} = 390$ kHz was fitted with a

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Table 1. Rotational transitions of gauche butyronitrile.

$J'_{K_-'K_+'} - J'_{K_-K_+}$	$F - F$	ν_{obs} (MHz)	$\nu_{unsplit}$ (MHz)	$\Delta\nu_{HFS\ obs}$ (kHz)	$\Delta\nu_{HFS\ obs-calc}$ (kHz)
$2_{12} - 1_{11}$	3 — 2	11 384.169	11 384.045	542	— 1
	2 — 1	11 383.627			
$2_{02} - 1_{01}$	3 — 2	11 912.707	11 912.654	84	21
	2 — 1	19 912.623			
$2_{11} - 1_{10}$	3 — 2	12 508.451	12 508.374	493	— 3
	2 — 1	12 507.958			
$3_{13} - 2_{12}$	4 — 3	17 055.664	17 055.590	198	27
	3 — 2	17 055.466			
$3_{03} - 2_{02}$ [a]	4 — 3	17 785.939	17 785.949	583	— 3
	3 — 2				
	2 — 1				
	3 — 3	17 785.356			
$3_{22} - 2_{21}$ [a]	4 — 3	17 919.837	17 919.629	625	— 2
	2 — 1				
	3 — 2	17 919.212			
	2 — 2				
$4_{13} - 4_{04}$	4 — 4	10 287.013	10 286.601	555	— 5
	5 — 5	10 286.458		158	14
	3 — 3	10 286.300			
$5_{14} - 5_{05}$	5 — 5	12 168.291	12 167.870	576	— 5
	6 — 6	12 167.715		133	14
	4 — 4	12 167.582			
$6_{15} - 6_{06}$	6 — 6	14 609.842	14 609.400	608	— 2
	7 — 7	14 609.234		126	23
	5 — 5	14 609.108			

[a] Stark measurement.

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Table 2. Rotational transitions of trans butyronitrile.

$J'_{K_-'K_+'} - J_{K_-K_+}$	$F' - F$	ν_{obs} (MHz)	$\nu_{unsplit}$ (MHz)	$\Delta\nu_{HFS\ obs}$ (kHz)	$\Delta\nu_{HFS\ obs-calc}$ (kHz)
$2_{12} - 1_{11}$	3 — 2	8 727.287	8 727.068	1074	8
	2 — 1	8 726.213			
$2_{02} - 1_{01}$	3 — 2	8 841.829	8 841.749	88	14
	2 — 1	8 841.741			
$2_{11} - 1_{10}$	3 — 2	8 957.630	8 957.437	1039	— 11
	2 — 1	8 956.591			
$3_{13} - 2_{12}$	4 — 3	13 090.425	13 090.312	352	53
	2 — 1				
	3 — 2	13 090.073			
$3_{13} - 2_{12}$[a]	2 — 2	13 091.424	13 090.319	1025	12
	4 — 3	13 090.399			
	2 — 1				
$3_{12} - 2_{11}$	4 — 3	13 435.954	13 435.846	337	32
	2 — 1				
	3 — 2	13 435.617			
$3_{12} - 2_{11}$[a]	2 — 2	13 436.570	13 435.801	673	— 9
	4 — 3	13 435.897			
	2 — 1				
$4_{14} - 3_{13}$[a]	3 — 3	17 454.461	17 453.162	1293	— 23
	5 — 4				
	4 — 3	17 453.168			
	3 — 2				

[a] Stark measurement.

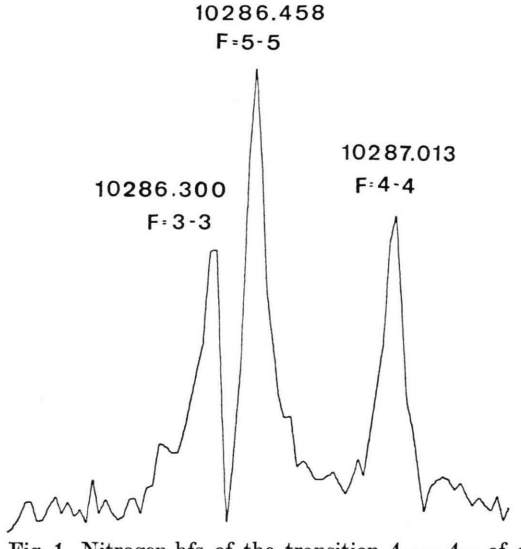

Fig. 1. Nitrogen-hfs of the transition $4_{13} - 4_{04}$ of gauche butyronitrile measured with MWFT spectroscopy. The power spectrum is drawn. Transient emissions recorded in steps of 20 ns for 1024 points. Measuring time approx 5 minutes for a 25 MHz range. Spectral points at 25 kHz distance. Frequency calculated by three points interpolation Lorentz profile assumed. Pressure 0.35 mT, temperature — 60 °C.

Table 3. Nitrogen quadrupole coupling constants of butyronitrile (MHz). The errors are standard errors.

	Trans form	Gauche form
$\chi^+ = \chi_{bb} + \chi_{cc}$	3.405 (45)	1.672 (22)
$\chi^- = \chi_{bb} - \chi_{cc}$	— 0.723 (77)	— 2.197 (35)
correlation coefficient (χ^+, χ^-)	0.282	0.120
derived constants		
χ_{aa}	— 3.405 (45)	— 1.672 (22)
χ_{bb}	1.341 (50)	— 0.263 (22)
χ_{cc}	2.064 (39)	1.935 (20)

mean square deviation $\sigma = 15$ kHz, the corresponding values for trans form are: $\overline{\Delta\nu} = 735$ kHz and $\sigma = 29$ kHz.

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