Nitrogen Hyperfine Structure in Allylcyanide Synperiplanar

An Application of Microwave Fourier Transform Spectroscopy

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With the help of Microwave Fourier transform Spectroscopy we were able to resolve the nitrogen hyperfine structure of allylcyanide synperiplanar (cis). As the rotational relaxation is relatively rapid this molecule is even for this technique at the limit of the present possibilities.

The microwave spectrum of allylcyanide, $CH_2=CHCH_2CN$, in its syn- and antiperiplanar (cis and trans) conformation was first investigated by Sastry et al. [1]. It was not possible to resolve the nitrogen hyperfine structure (hfs) by Stark spectroscopy. By use of Microwave Fourier transform (MWFT) spectroscopy [2–4] in the range of 5 to 18 GHz we succeeded to resolve the hfs pattern of rotational transitions of allylcyanide synperiplanar.

The sample was purchased with 98% purity from Ega Chemie, Steinheim, and used without further purification. The spectra were taken at a temperature of 230 K and pressures down to 0.1 mTorr.

Table 1. Measured transitions [MHz] of allylcyanide synperiplanar, ν_{FT}: unresolved or calculated unsplit line frequencies by MWFT spectroscopy, ν_{Stark}: frequencies by MW Stark spectroscopy, ν[1]: by Ref. [1].

$J_{K-K_+} - J'_{K'-K'_+}$	ν_{FT}	ν_{Stark}	$\nu_{[1]}$
$1_{11} - 0_{00}$	14 181.420	14 181.578	14 181.35
$2_{02} - 1_{01}$	13 123.310	13 123.322	
$2_{11} - 1_{10}$	14 076.500	14 076.554	14 076.17
$2_{12} - 1_{11}$	12 314.966		12 314.24
$2_{20} - 2_{11}$		22 823.322	
$2_{11} - 2_{02}$	9 417.608		9 417.78
$2_{21} - 2_{12}$		25 392.998	
$2_{12} - 1_{01}$		19 898.628	19 898.50
$3_{03} - 2_{02}$		19 507.120	19 506.65
$3_{13} - 2_{12}$		18 428.852	18 428.50
$3_{12} - 3_{03}$	10 977.747		10 978.03
$3_{03} - 2_{12}$	12 731.874	12 731.866	12 731.42

Table 2. Resolved hfs multiplets ν_{exp} [MHz] of allylcyanide synperiplanar. ν_{FT}: calculated unsplit line, $\Delta\nu_{exp}$, $\Delta\nu_{calc}$ [MHz]: experimental and calculated hfs splittings.

$J_{K-K_+} - J'_{K'-K'_+}$	$F-F'$	ν_{exp}	ν_{FT}	$\Delta\nu_{exp}$	$\Delta\nu_{calc}$
$2_{11} - 1_{10}$	1–0	14077.439			
				0.724	0.779
	2–2	14076.715			
				0.144	0.091
	3–2	14076.571	14076.500		
				0.515	0.523
	2–1	14076.056			
				0.152	0.142
	1–1	14075.904			
$2_{12} - 1_{11}$	1–0	12315.364			
				0.251	0.238
	3–2	12315.113	12314.966		
				0.559	0.573
	2–1	12314.554			
$2_{11} - 2_{02}$	1–1	9417.050			
				0.406	0.387
	3–3	9417.456	9417.608		
				0.706	0.696
	2–2	9418.162			
$3_{12} - 3_{03}$	2–2	10977.369			
				0.229	0.217
	4–4	10977.598	10977.747		
				0.615	0.620
	3–3	10978.213			
$4_{13} - 4_{14}$	3–3	8780.693			
				0.233	0.203
	5–5	8780.926	8781.119		
				0.767	0.788
	4–4	8781.693			
$8_{26} - 8_{27}$	7–7	11474.978			
				0.072	0.058
	9–9	11475.050	11475.183		
				0.464	0.458
	8–8	11475.514			
$8_{54} - 9_{45}$	7–8	11549.425			
				0.044	0.032
	9–10	11549.469	11549.549		
				0.271	0.274
	8–9	11549.740			
$11_{38} - 11_{39}$	10–10	8409.317			0.025
	12–12	8409.317	8409.417		
				0.299	0.275
	11–11	8409.616			

We checked first the assignment by repeating some measurements with Stark spectroscopy given in Table 1, column 3. The hfs was not resolved. The frequencies differ from those of [1] (Table 1, column 4) sometimes by more than 300 kHz. The agreement with our MWFT measurements (Table 1, column 2) is better.

For the resolved lines the frequencies ν_{FT} were calculated from the hfs pattern by adding the cal-

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Table 3. Rotational and quadrupole coupling [MHz] constants of allylcyanide synperiplanar. $\varkappa$: asymetry parameter; σ: standard deviation of the fit [kHz]; $|(\chi^+, \chi^-)|$: correlation coefficient.

A	11323.008 (65)	$\chi^+ = \chi_{bb} + \chi_{cc}$	1.763 (34)	χ_{aa}	−1.763 (34)
B	3739.297 (16)	$\chi^- = \chi_{bb} - \chi_{cc}$	−2.331 (36)	χ_{bb}	−0.284 (35)
C	2858.522 (19)	$\|(\chi_{bb}, \chi_{cc})\|$	0.1	χ_{cc}	2.047 (35)
$\varkappa$	−0.791889				
σ	78				

culated hfs shifts to the frequencies of the components and taking the mean value. These mean values agree within the measuring error with the intensity weighted means.

In Table 3 we give the rotational constants for the rigid rotor model. The standard deviation of the fit for the Fourier transform measurement is 78 kHz. The highest correlation is $|(A, C)| = 0.6$. Rotational constants calculated from our Stark measurements ν_{stark} agree within the error limits, but the standard deviation is 114 kHz.

In Table 2 we give the frequencies of the resolved hfs patterns. The measurements were difficult as the transient decay was rapid as two strong dipole moment components exist. The measurement of the $1_{01}-0_{00}$ at 6597.819 MHz and $1_{11}-0_{00}$ at 14 181.420 MHz was disturbed by nearby strong transitions. The splittings were analysed by first order hfs theory [5]. This approximation was checked by a program using direct diagonalisation of an appropriate Hamiltonian submatrix [6].

It was further proved that the off diagonal element χ_{ab} of the coupling tensor is without influence. The quadrupole coupling constants are given in Table 3. The standard deviation of the fit is 18 kHz, the mean splitting 354 kHz, the correlation is 0.1.

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