Deuterium Quadrupole Coupling in Cyanoacetylene

An Application of Microwave Fourier Transform Spectroscopy

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Only few molecules have been investigated for deuterium hyperfinestructure (d-hfs) by microwave spectroscopy. The d-hfs of some additional molecules was analysed by beam methods (beam maser spectroscopy, molecular beam electric resonance spectroscopy). For a detailed bibliography see Landolt-Börnstein [1, 2].

By use of Microwave Fourier transform Spectroscopy [3, 4] we are able to increase the resolution of standard microwave spectroscopy because modulation and saturation broadening effects are avoided. Also Stark broadening by imperfect biasing of the Stark square wave is not present. With our spectrometer we are able to measure at low pressures. Pressure broadening can thus be minimized. Doppler and wall broadening are now limiting the resolution of our instrument.

We investigated the $J = 1 - 0$ and $2 - 1$ transitions of cyanodeuteroacetylene-^{15}N, $D - C \equiv C - C^{15}N$. The prediction of the transitions was based on measurements of Mallinson and de Zafra [5].

The sample of $D - C \equiv C - C^{15}N$ was prepared by one of us (M.A.) by modifying published procedures [6, 7].

A sample of propynoic acid methyl ester (0.84 g) $H - C \equiv C - CO_2CH_3$ from EGA CHEMIE, Steinheim, was dissolved in 2 ml of methanol and 2 ml D_2O. The mixture was allowed to react at 213 K with liquid-ammonia ^{15}N (0.34 g) from IC-Chemikalien München. After one hour of vigorous stirring the volatile products were pumped off at 1 mTorr until the product was very dry. The amide $D - C \equiv C - CO^{15}NH_2$ was then dissolved in a

second sample of D_2O (99%) for 16 hours. After pumping off D_2O the resulting product was slowly heated up to 453 K with 16 g sand and 10 g P_2O_5. The yield of deuterocyanoacetylene-^{15}N was 0.25 g (about 50%).

The results of the measurements are given in Table 1. In Fig. 1 the hfs of the $J = 1 - 0$ line is shown.

Table 1. Measured lines [MHz] of cyanodeuteroacetylene with deuterium hfs. $\bar{\nu}$ Intensity weighted mean frequency, measuring accuracy 5 kHz. $\Delta\nu_{calc}$ calculated with $eqQ = 229.6$ kHz.

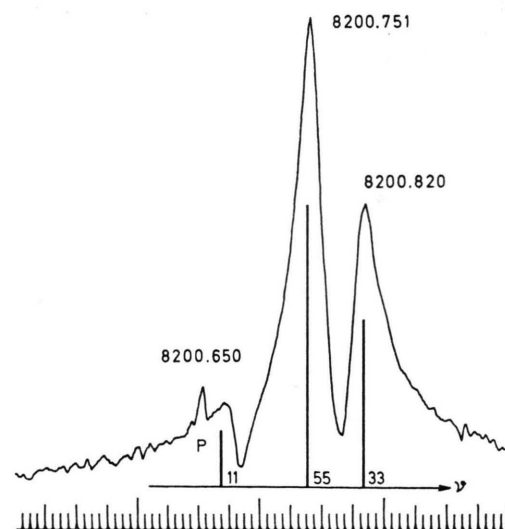| $J - J'$	$F - F'$	ν_{exp}	$\bar{\nu}$	$\Delta\nu_{exp}$	$\Delta\nu_{calc}$
1 − 0	1 − 1	8200.820		69	68.9
	2 − 1	8200.751	8200.763		
	0 − 1	8200.650		101	103.3
2 − 1	2 − 2	16401.581			
	1 − 0				
	2 − 1	16401.513	16401.516	68	65.5
	3 − 2				
	1 − 1	16401.400		113	111.6

Fig. 1. A section out of a 5 MHz scan of the rotational spectrum of cyanodeuteroacetylene-^{15}N, $J = 1$–0 with the theoretical pattern with relative intensities. The transient emission signal was recorded with a sample interval of 100 ns and 1024 data points. Measuring time 25 min., 3×10^6 averaging cycles. Prior to the Fourier transformation the time domain signal was extended to 2048 data points by zeros. Spectral points at 5 kHz distance. Pressure 0.2 mTorr, temperature 213 K. Marker distance 9.37 kHz. P perturbing signal.

A straightforward analysis [8] results in the rotational constant B_0 and the quadrupole coupling constant $e\,q\,Q$ in Table 2.

Our $e\,q\,Q$ value compares with the coupling constants of other acetylene compounds (Table 3).

The rotational constant which we determined from the two lowest rotational transitions, differs from that measured by [5]. They based their computation of B_0 and seven additional constants on eight

Table 2. Rotational and quadrupole coupling constants of cyanodeuteroacetylene-^{15}N with standard errors.

$B_0 = 4100.380 \pm 0.002$ MHz,
$eqQ = 229.6 \quad \pm 4.8 \quad$ kHz.

Table 3. Comparison of deuterium quadrupole coupling constants [kHz] of acetylene compounds.

DC $\equiv$ C$-$F	212	$\pm$ 10	[9]
DC $\equiv$ C$-$Cl	225	$\pm$ 18	[9]
DC $\equiv$ C$-$CH$_3$	208	$\pm$ 10	[9]
DC $\equiv$ C$-$CN	229.6	$\pm$ 4.8	this work

rotational transitions $J = 3 - 4$ in different vibrational states.

The hfs of cyanodeuteroacetylene-^{14}N, containing two quadrupole nuclei, is presently under investigation.

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Erratum

I want to bring to the attention of our readers that the paper by Ke-Hsueh Li, Z. Naturforsch. 36 a, 813 [1981], has been printed without having been reviewed by the editors.

A. Klemm