Nitrogen-14 Nuclear Quadrupole Coupling and Centrifugal Distortion of Pivalonitrile

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The rotational transitions $J' - J'' = 1-0$, $2-1$, $3-2$, and $4-3$ of pivalonitrile have been measured in the frequency range of 5–22 GHz with a microwave Fourier transform spectrometer. The ^{14}N nuclear quadrupole coupling constant, $e\,q\,Q$, as well as the centrifugal distortion parameters, D_J and D_{JK}, have been determined to be: $e\,q\,Q = -4.221\,(15)$ MHz; $D_J = 0.349\,(56)$ kHz, $D_{JK} = 3.68\,(15)$ kHz. The rotational constant B_0 was fixed with high precision: $B_0 = 2749.9093\,(13)$ MHz. Nitrogen-14 quadrupole coupling in pivalonitrile is compared with that in other cyano compounds.

Pivalonitrile (tertiary butyl cyanide, trimethyl acetonitrile) was first investigated in the microwave region by Sparstad and Amble [1], Zeil and Pfrommer [2], and Bak, Hansen-Nygaard, and Rastrup-Andersen [3] with the main objective to determine the structure and especially the $\geqslant$C$-$C$\equiv$ distance of the molecule. The most detailed and most precise work on pivalonitrile up to now was published later by Nugent, Mann, and Lide, Jr. [4]. In that work they measured the dipole moment and calculated a partial r_s-structure. The determination of the $\geqslant$C$-$C$\equiv$ distance was a contribution to the discussion about the effects of hyperconjugation on C$-$C-bond lengths. All previous authors used Stark-effect modulated spectrometers and did not succeed in resolving either the ^{14}N nuclear quadrupole hyperfine structure (^{14}N-hfs) or the K fine structure of the rotational lines. So we employed microwave Fourier transform (MWFT) technique to see the multiplets and to obtain, for a comparison with related species, the ^{14}N quadrupole coupling constant. As a kind of by-product we further got a better refined rotational constant and the centrifugal distortion parameters. Recently, two millimetre-wave studies of pivalonitrile have been reported [5, 6] leading to accurate values of the rotational constant and centrifugal distortion constants.

Because of the large dipole moment ($\mu = 3.97\,(5)$ D [4]) and the resulting strong dipole-dipole interaction between molecules in the gaseous sample, the decay of the molecular signal, induced by macroscopic polarization, is proceeding much faster compared to "normal" molecules. This leads, after Fourier transformation, to an increased line width and with that to a reduced resolution in the frequency domain. To be able to make use of the resolving capability of MWFT spectroscopy nevertheless, one has to perform the experiments at very low pressures trying to find a compromise between too weak signals as a result of the decreasing number of molecules in the waveguide cell and too broad lines as a result of the dipole-dipole interaction. Fortunately, we succeeded in achieving a still sufficient resolution.

The sample was obtained commercially from Aldrich-Chemie, Steinheim, F.R.G., with 98% purity, and was used without further purification. We did the measurements at Kiel with four different types of the MWFT spectrometer in J- [7], X- [8], Ku- [9], and K-band [10], i.e., in the frequency range of 5–22 GHz, with waveguide sample cells corresponding to the nominal frequency band, respectively, at temperatures ranging from $-60\,°$C to room temperature and pressures below 0.5 mTorr. Two examples, the first one with a Gauss convolution in the time domain for noise reduction, are given in Figs. 1 and 2. The experimental frequencies, their assignments (following the selection rules

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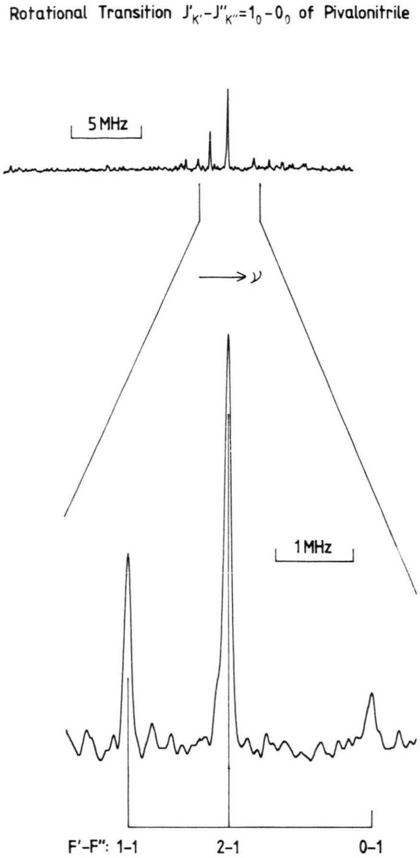

Fig. 1. Nitrogen-14 nuclear quadrupole hyperfine structure of the $1_0 - 0_0$ rotational transition of pivalonitrile.
Upper trace: A 25 MHz range of the microwave power spectrum. The decaying molecular signal has been recorded with a sample interval of 20 nsec and 9600 k pulse experiments in the time domain. In order to improve the signal to noise ratio by cutting the noise in the last part of the time dependent recording, where we nearly do not have a molecular signal any more, the 1024 data points were, prior to Fourier transformation, convoluted, i.e., multiplied, with an appropriately sloping Gauss-function. But none the less there is a small fading molecular signal in that part of the recording, so that we have to pay for the achieved gain in relative line intensity with a slightly increased line width in the frequency domain. For a smooth interpolation of the frequency spectrum the data points were supplemented by zeros to give 4 k points prior to and 2 k points after Fourier transformation. Microwave polarizing frequency: 5504 MHz; sample gas pressure: 0.18 mTorr; temperature in the waveguide cell: $-51\,^{\circ}$C.
Lower trace: A 4.5 MHz range of the upper chart frequency spectrum. The calculated intensities of the ^{14}N-hfs components have been drawn in as stroke pattern.

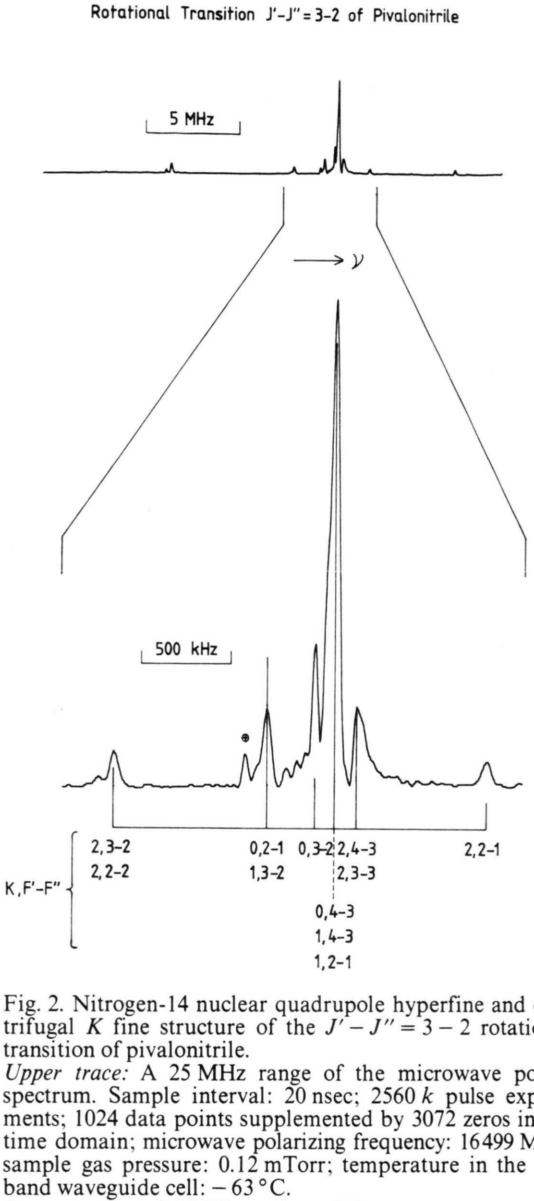

Fig. 2. Nitrogen-14 nuclear quadrupole hyperfine and centrifugal K fine structure of the $J' - J'' = 3 - 2$ rotational transition of pivalonitrile.
Upper trace: A 25 MHz range of the microwave power spectrum. Sample interval: 20 nsec; 2560 k pulse experiments; 1024 data points supplemented by 3072 zeros in the time domain; microwave polarizing frequency: 16499 MHz; sample gas pressure: 0.12 mTorr; temperature in the Ku-band waveguide cell: $-63\,^{\circ}$C.
Lower trace: A 2.6 MHz section of the upper trace recording with the $3 - 2$ rotational line. ⊕: coherent disturbing signal at the polarizing frequency $\nu = 16499$ MHz. The expected ^{14}N-hfs and K component intensities, summed up according to the composition of the experimental lines and squared because of the power spectrum, have been plotted as stroke pattern. We attribute the disagreement between expected and experimental intensities to differing polarizing conditions.

Table 1. Experimental frequencies of pivalonitrile and their deviations from a centrifugal distortion and ^{14}N-hfs fitting calculation. ν_{exp}: experimental frequency; w: squared calculated intensity of the respective component of the rotational transition, normalized to one for the total composite experimental line. The relative proton spin weights 176 : 352 : 336 for $K = 0$, $K = \pm 3$, and $K = \pm 1, \pm 2$ have been included. ν_0: hypothetical frequency of the unsplit K-line. Frequencies and deviations in MHz. The level with the higher energy value is marked with a single prime.

$J' - J''$	K	$F' - F''$	ν_{exp}	w	$\delta_{\text{calc-exp}}$	$\bar{\nu}_0$
1 − 0	0	2 − 1	5500.028	1.000	0.003	5499.817
	0	1 − 1	5498.770	1.000	0.008	
	0	0 − 1	5501.922	1.000	−0.006	
2 − 1	0	3 − 2	10999.722	1.000	0.006	10999.626
	0	2 − 1	10999.607	0.813	−0.019	
	0	1 − 0	10998.557	0.087	−0.014	
	1	3 − 2	10999.875	1.000	0.008	10999.611
	1	2 − 1	10998.557	0.913	0.001	
	1	1 − 1	10999.607	0.188	−0.005	
3 − 2	0	4 − 3	16499.516	0.219	0.048	16499.418
	0	3 − 2	16499.404	1.000	−0.014	
	0	2 − 1	16499.130	0.135	−0.077	
	1	4 − 3	16499.516	0.641	0.007	16499.396
	1	3 − 2	16499.130	0.865	−0.002	
	1	2 − 1	16499.516	0.140	0.015	
	2	4 − 3	16499.645	0.993	0.014	16499.330
	2	3 − 2	16498.276	0.985	0.002	
	2	2 − 1	16500.378	1.000	−0.007	
	2	3 − 3	16499.645	0.007	0.014	
	2	2 − 2	16498.276	0.015	0.002	
4 − 3	0	5 − 4	21999.234	0.107	0.017	21999.185
	0	4 − 3	21999.160	0.347	−0.025	
	0	3 − 2	21999.043	0.152	−0.051	
	1	5 − 4	21999.234	0.346	0.016	21999.156
	1	4 − 3	21999.043	0.848	−0.007	
	1	3 − 2	21999.160	0.653	−0.003	
	1	4 − 4	21997.956	0.005	−0.039	
	2	5 − 4	21999.234	0.221	0.014	21999.067
	2	4 − 3	21998.646	0.996	0.001	
	2	3 − 2	21999.401	0.992	0.033	
	2	4 − 4	21998.646	0.004	0.001	
	2	3 − 3	21999.401	0.008	0.033	
	3	5 − 4	21999.234	0.327	0.009	21998.920
	3	4 − 3	21997.956	0.995	−0.014	
	3	3 − 2	21999.702	0.992	−0.009	
	3	4 − 4	21999.702	0.008	−0.027	

$\Delta J = +1$, $\Delta K = 0$, and $\Delta F = 0, \pm 1$ of a symmetric top molecule), and their deviations from theoretical calculations are contained in Table 1. The uncertainty in experimental frequency determination is estimated to be 10−20 kHz.

The rotational lines and their components could easily be assigned by taking the rotational constant B_0 from the literature [4], taking the ^{14}N quadrupole coupling constant $e\,q\,Q$ from related molecules (e.g. from CH_3CN [11]), and initially putting to zero the centrifugal distortion parameters. We then fitted the rotational constant B_0, the centrifugal distortion parameters D_J and D_{JK}, and the nitrogen-14 nuclear quadrupole coupling constant $e\,q\,Q$ to the experimental frequencies according to second order perturbation theory* using the well-known expressions for the rotational frequencies of a centrifugally distorted symmetric top molecule [12],

$$\nu = 2 B_0 (J+1) - 4 D_J (J+1)^3 - 2 D_{JK} (J+1) K^2, \quad (1)$$

and the additional energy, resulting from the interaction of the quadrupole nucleus with the electron cloud during overall rotation of the molecule. We used the first order expression [13],

$$E_Q = e\,q\,Q \left[\frac{3\,K^2}{J\,(J+1)} - 1 \right] Y(J, I, F), \quad (2)$$

$Y(J, I, F)$ being Casimir's function, and second order contributions [14]. The results of our analysis are comprised in Table 2. The centrifugal distortion constants D_J and D_{JK} turn out to be extremely small, but these constants and the rotational constant B_0 are in good agreement with the more ac-

Table 2. Rotational constant B_0, centrifugal distortion parameters D_J and D_{JK}, and ^{14}N nuclear quadrupole coupling constant $e\,q\,Q$ of pivalonitrile as results of a least squares fit to the experimental frequencies. All values in MHz, single standard deviations in brackets. N: number of rotational lines used for the fit, N_{comp}: number of underlying K- and ^{14}N-hfs components; σ: standard deviation of the fit. The more accurate B_0-, D_J-, and D_{JK}-mm-wave values have been added for comparison.

	This work	Correlation matrix				[5]	[6] Fit II
B_0	2749.9093 (13)	1.00				2749.9089 (10)	2749.90955 (25)
D_J	0.000349 (56)	0.88	1.00			0.0003138 (14)	0.00031878 (38)
D_{JK}	0.00368 (15)	−0.08	−0.45	1.00		0.003826 (12)	0.0038524 (24)
$e\,q\,Q$	−4.221 (15)	0.03	0.04	−0.02	1.00		
N	4						
N_{comp}	36						
σ	0.012						

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* Programs DRTSHZ for the prospection of lines and FRTSHZ for fitting the molecular parameters to the experimental data by Dr. U. Andresen, Kiel, F.R.G.

curate mm-wave values [5, 6], which, for comparison, are also given in Table 2. As we fitted four parameters, the standard deviation of the fit was calculated according to

$$\sigma = \sqrt{\frac{1}{N_{\mathrm{comp}} - 4} \sum_{i=1}^{N_{\mathrm{comp}}} (\delta^{(i)}_{\mathrm{calc-exp}})^2} \qquad (3)$$

(for an explanation of the symbols see Tables 1 and 2!).

When comparing ^{14}N quadrupole coupling in related molecules, it has to be stated that the value we found for pivalonitrile ($e\,q\,Q = -4.221\,(15)$ MHz) is in close agreement with the ^{14}N quadrupole coupling constants reported for CH_3CN ($e\,q\,Q = -4.2244\,(15)$ MHz [11]), CH_3CH_2CN ($\chi_{zz} = -4.14(4)$ MHz [15, 16, 17]), and C_6H_5CN ($\chi_{zz} = \chi_{aa} = -4.187\,(16)$ MHz [18]), whereas in the cases of $H_2C(CN)_2$ ($\chi_{zz} = -4.10\,(4)$ MHz [19]) and $D-C \equiv C-CN$ ($e\,q\,Q = -4.316\,(3)$ MHz [20]) for example, the differences are somewhat greater due to a different charge distribution about ^{14}N. In all these cases the CN group is shown to be rather insensitive to substituent effects as regards nitrogen-14 quadrupole coupling.

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