^{14}N Quadrupole Coupling in the Rotational Spectra of Cyclopropylamine and Cyclopropyl Cyanide

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To Prof. Dr. H.D. Rudolph on Occasion of his 65th Birthday

The ^{14}N hyperfine structure in the rotational spectra of cyclopropylamine and cyclopropyl cyanide has been reinvestigated by microwave Fourier transform spectroscopy. The observed quadrupole coupling constants in units of MHz are: $X_{aa} = 2.3338(18)$, $X_{bb} = 1.7874(20)$, $X_{cc} = -4.1209(20)$ for cyclopropylamine and $X_{aa} = -3.4536(35)$, $X_{bb} = 1.7468(51)$, $X_{cc} = 1.7068(51)$ for cyclopropyl cyanide.

Key words: Cyclopropylamine, Cyclopropyl cyanide, ^{14}N quadrupole coupling.

Introduction

The ^{14}N hyperfine structure in the rotational spectra of cyclopropylamine and cyclopropyl cyanide was first studied by Carvallo [1]. Later Brown et al. [2] analyzed the hyperfine patterns under improved resolution. In view of our interest in the molecular Zeeman effect of small ring compounds we reinvestigated the zero field spectra of both molecules under even greater resolution. Knowledge of accurate quadrupole coupling constants is a prerequisite for a subsequent study of the Zeeman hfs multiplets in strong magnetic field.

Experimental Details and Analysis

The samples (95%) were purchased from Aldrich Chemie Steinheim, West Germany and were used after several bulb to bulb distillations without further purification. Both molecules show an *a*- and a *c*-type spectrum. No *b*-type spectrum is observed since the *b*-component of the electric dipole moment is zero by symmetry (Figure 1). The spectra were taken with our high resolution time domain spectrometers [3, 4]. Our observed frequencies are given in Tables 1 and 2. Typical sample pressures were in the range between 0.5 and 2 mTorr at temperatures close to 220 K. For the analysis of the observed splittings the energies were calculated within the coupled basis $|J, K_a, K_c, I, F, M_F\rangle$ neglecting all matrix elements off-diagonal in J and $K_a K_c$ [5]. Also spin-rotation interaction was neglected.

The quadrupole coupling constants were fitted to the observed hfs frequencies in an iterative procedure. In the first step of each iteration cycle the positions of the hfs satellites with respect to the hypothetical center frequencies of the transitions were calculated from the approximate coupling constants determined in the previous cycle. Each of these calculated splittings was then used to recalculate the corresponding center frequency.

This leads to as many "center frequencies" as there are experimental satellite frequencies. There is very little scatter in the center frequency if the quadrupole coupling constants are already good; the scatter is much larger if they still need improvement. Then for each multiplet the hfs satellite intensity weighted mean of these calculated center frequencies was taken as the new hypothetical center frequency. Finally, to complete the cycle, improved quadrupole coupling constants were calculated by a least squares fit of the splittings of the observed hfs satellite frequencies of each multiplet with respect to the corresponding intensity weighted mean center frequency. These cycles were repeated until the results stabilized. Our final quadrupole coupling constants are given in Table 3.

We note that the transient emission signals were analyzed using the decay-fit routine developed by Haekel and Mäder [6] at Kiel University. Traditional Fourier transform analysis of the observed decays would have been impractical because of closely spaced molecular resonances. (The typical problems, which arise when

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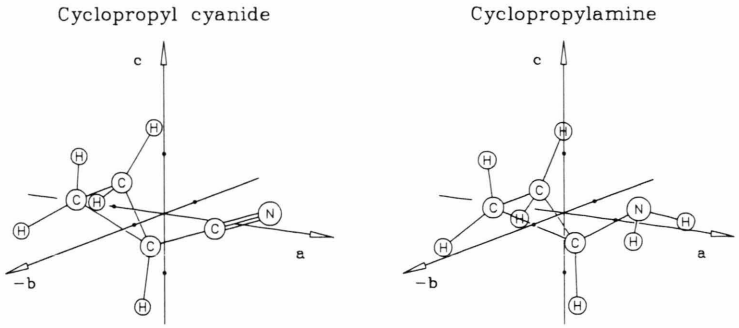


Fig. 1. Orientation of the principle inertia axes in cyclopropyl cyanide and cyclopropylamine. Both molecules show mirror symmetry with respect to the *a*, *c*-plane.

Table 1. Measured rotational transitions of cyclopropylamine. Also given are the relative intensities as they would be observed in a cw spectrometer. All frequencies are given in MHz.

$J'_{K_a K_c} \rightarrow J_{K_a K_c}$ Center frequency	$F' \rightarrow F$	Frequency	Splitting obs.	Splitting calc.	INT/ %
$1_{01} \rightarrow 0_{00}$					
	2–1	12 518.287	−.117	−.117	55.6
12 518.404(2)	1–1	12 518.985	.581	.583	33.3
	0–1	12 517.251	−1.153	−1.167	11.1
$1_{11} \rightarrow 1_{01}$					
	2–2	9 547.119	.028	.027	41.7
9 547.091(1)	1–2	9 547.654	.563	.564	13.9
	2–1	9 546.421	−.673	−.673	13.9
	0–1	9 545.613	−1.478	−1.477	11.1
	1–0	9 548.702	1.614	1.614	11.1
	1–1	9 546.956	−.135	−.137	8.3
$2_{02} \rightarrow 1_{10}$					
	3–2	14 497.205	−.392	−.392	46.7
14 497.598(1)	2–1	14 499.277	1.680	1.680	25.0
	1–0	14 494.889	−2.709	−2.710	11.1
	2–2	14 498.041	.444	.444	8.3
	1–1	14 497.979	.382	.381	8.3
$2_{12} \rightarrow 2_{02}$					
	3–3	8 683.655	−.108	−.109	41.5
8 683.764(2)	2–2	8 684.142	.379	.381	23.1
	1–1	8 683.385	−.379	−.381	15.0
	1–2	8 685.444	1.680	1.680	5.0
	2–1	8 682.070	−1.694	−1.680	5.0
	2–3	8 682.826	−.938	−.944	5.0
	3–2	8 684.984	1.220	1.216	5.0
$3_{12} \rightarrow 2_{20}$					
	4–3	10 199.127	−.092	−.093	42.9
10 199.219(2)	3–2	10 199.591	.372	.371	29.7
	2–1	10 198.790	−.429	−.427	20.0
$4_{14} \rightarrow 3_{22}$					
	5–4	15 241.947	−.467	−.466	40.8
15 242.414(1)	4–3	15 243.697	1.283	1.283	31.3
	3–2	15 241.497	−.917	−.916	23.8
	4–4	15 243.697	1.283	1.283	2.1
	3–3	15 241.497	−.917	−.916	2.1
$4_{13} \rightarrow 4_{14}$					
	5–5	9 257.613	.532	.534	41.7
9 257.081(3)	4–4	9 255.612	−1.469	−1.469	32.3
	3–3	9 258.135	1.054	1.049	26.0
$5_{24} \rightarrow 4_{32}$					
	6–5	12 183.916	−.240	−.242	40.3
12 184.156(2)	5–4	12 184.794	.638	.642	33.0
	4–3	12 183.719	−.437	−.440	26.7

Table 2. Measured rotational transitions of cyclopropyl cyanide. Also given are the relative intensities as they would be observed in a cw spectrometer. All frequencies are given in MHz.

$J'_{K_a K_c} \rightarrow J_{K_a K_c}$ Center frequency	$F' \rightarrow F$	Frequency	Splitting obs.	Splitting calc.	INT/ %
$1_{01} \rightarrow 0_{00}$					
	2–1	6 751.535	.173	.173	55.6
6 751.362(1)	1–1	6 750.499	−.863	−.863	33.3
	0–0	6 753.089	1.727	1.727	11.1
$2_{02} \rightarrow 1_{01}$					
	3–2	13 500.837	.075	.074	46.7
13 500.762(1)	2–1	13 500.762	.000	.000	25.0
	1–0	13 499.896	−.866	−.864	11.1
	2–2	13 499.721	−1.041	−1.036	8.3
	1–1	13 502.493	1.731	1.727	8.3
$2_{11} \rightarrow 1_{10}$					
	3–2	13 681.771	.212	.210	46.7
13 681.559(2)	2–1	13 680.700	−.859	−.863	25.0
	1–0	13 682.852	1.293	1.290	11.1
	1–1	13 681.563	.004	.010	8.3
	2–2	13 681.204	−.355	−.351	8.3
$2_{12} \rightarrow 1_{11}$					
	3–2	13 324.034	.208	.209	46.7
13 323.826(2)	2–1	13 322.964	−.862	−.863	25.0
	1–0	13 325.132	1.306	1.300	11.1
	1–1	13 323.813	−.013	−.010	8.3
	2–2	13 323.493	−.333	−.339	8.3
$4_{04} \rightarrow 3_{12}$					
	5–4	14 030.522	.096	.096	40.8
14 030.426(1)	4–3	14 030.213	−.213	−.210	31.3
	3–2	14 030.522	.096	.094	23.8

Table 3. Rotational constants and quadrupole coupling constants [MHz] of cyclopropylamine and cyclopropyl cyanide. Numbers in parentheses are one standard deviation in units of the least significant figures. The rotational constants result from a rigid rotor fit to the hypopthetical center frequencies of the hfs multiplets (compare Tables 1 and 2).

	a) Cyclopropylamine	b) Cyclopropyl cyanide
A	16 270.159 (13)	15 786.270 (20)
B	6 723.041 (05)	3 465.107 (04)
C	5 795.339 (05)	3 286.241 (04)
X_{aa}	2.3338(18)	−3.4536(35)
X_{bb}	1.7872(20)	1.7468(51)
X_{cc}	−4.1209(20)	1.7068(51)

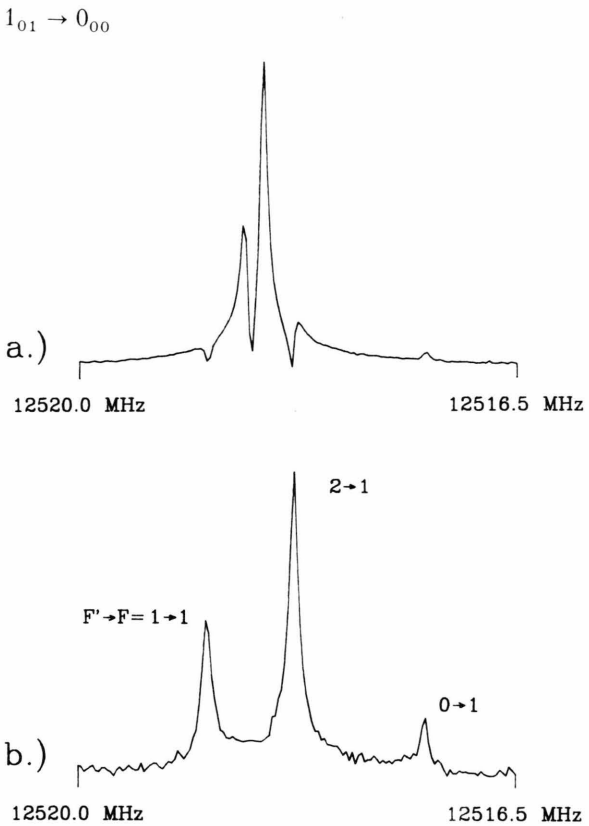
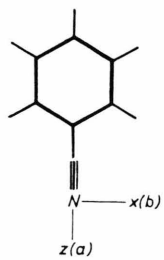
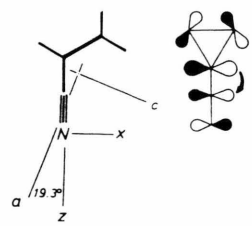


Fig. 2. Cyclopropylamine resonances in the vicinity of the $1_{01} \rightarrow 0_{00}$ rotational transition.
Trace a): A 3.5 MHz section out of a 50 MHz Fourier transform amplitude spectrum shows a total of five resonances. *Trace b):* After subtraction of the two strongest signals from the experimental decay using the decayfit routine [6], the $1_{01} \rightarrow 0_{00}$ ^{14}N hfs triplet clearly shows up in the Fourier transform amplitude spectrum of the residual.
Experimental data: Sample rate: 10 ns; sample points: 4096; temperature: 213 K; pressure: 1 mTorr; polarizing frequency: 12 518 MHz.

Table 4. Comparison of the anisotropy of the ^{14}N quadrupole coupling tensors of benzonitrile [10] and cyclopropyl cyanide (this work), demonstrating the excellent π-donor property of the cyclopropyl ring [13]. For cyclopropyl cyanide X_{xx} and X_{yy} follow from X_{aa} and X_{cc} under the assumption that the z-axis of the tensor is aligned to the C≡N bond. Uncertainties result from the experimental uncertainties and an assumed extra uncertainty of $\pm 1^\circ$ in the angle between the a-axis and the z-axis.

	Benzonitrile	Cyclopropyl cyanide
		
X_{xx}	2.290(3)	2.428(98)
X_{yy}	1.954(3)	1.747(05)
X_{zz}	−4.224(4)	−4.175(98)

the peaks in Fourier transform power spectra are directly used as molecular resonances, have been pointed out by Stolze and Sutter [7] and have been elaborated in detail by Böttcher and Sutter in the Appendix of their paper on the fluorobenzonitriles [8].) Some of the close by signals originate from hitherto unassigned lines. This is demonstrated in Figure 2. The upper trace shows a Fourier transform amplitude spectrum of the frequency range in which we expected to find the previously unmeasured hfs-triplet of the $1_{01} \rightarrow 0_{00}$ rotational transition of cylcopropylamine. At first glance the spectrum indeed shows a triplet with the expected intensity ratio. It also shows two minor additional features with only poorly determined frequencies. But when we included the strong triplet in our least squares fit of the quadrupole coupling, the quality of the fit deteriorated. Obviously the triplet used as input datum was too narrowly spaced. On the other hand, the small features did approximately fit the expected splittings. That they indeed were part of the $1_{01} \rightarrow 0_{00}$ triplet became dramatically obvious when, after the fit of all five signals, the two strongest yet unassigned signals were substracted from the observed transient emission. The amplitude spectrum of the resulting residual then clearly showed the $1_{01} \rightarrow 0_{00}$ triplet we were looking for (see lower trace in Figure 2). The final triplet frequencies resulting from the fit of all five resonances present in this frequency range are listed in Table 1 together with the hfs patterns of the other low-J transitions studied here. Our best fit for the rigid rotor rotational constants and the quadrupole coupling constants is presented in Table 3. The relative precision of the quadrupole coupling constants has been improved considerably. This makes them ideally suited for a test of the intramolecular electric field gradients at the nitrogen nucleus calculated by ab initio methods. Furthermore, the accurate quadrupole coupling constants and hfs-multiplet center frequencies determined here provide an excellent basis for a rotational Zeeman effect study currently under way in our laboratory.

We may also note that our results indicate that in cyclopropylamine, ^{14}N quadrupole coupling with its tensor axis aligned to the lone pair is very similar to the coupling in ammonia [9]. In cyclopropyl cyanide, however, the ^{14}N quadrupole coupling tensor, usually assumed to have cylindrical symmetry around the C≡N bond [10], shows an extreme anisotropy, which exceeds the anisotropy observed earlier for benzonitrile [11] approximately by a factor of two. This observation, which in a simplified MO picture [12] corresponds to an excess population in the out-of plane p_y-orbital at the nitrogen nucleus, is in perfect agreement with the assumption that the strained cyclopropyl ring is an excellent π-donor. The latter can be easily rationalized as the result of electron donation from the highest occupied molecular orbital (→ Walsh orbital) of cyclopropyl to the lowest unoccupied molecular orbital of the nitrile π-system, as has been discussed in detail by Harmony et al. [13]. The corresponding frontier molecular orbital model (Fig. 1 of [13]) is shown in the heading of Table 4.

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