^{14}N Quadrupole Coupling in the Rotational Spectra of 2,2,2-Trifluoroethylamine, Isopropylamine, and Aminoethanole

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We utilized the high resolution of microwave Fourier transform spectroscopy to investigate the ^{14}N-hyperfine structure of trans-2,2,2-trifluoroethylamine, $CF_3CH_2NH_2$, trans-isopropylamine, $CH_3CHNH_2CH_3$, and aminoethanole, $HOCH_2CH_2NH_2$, and the amino deuterated isotopomers trifluoroethylamine-d_2 and isopropylamine-d_2. The complete coupling tensor of trifluoroethylamine could be determined. We found that the fluorine atoms have a distinct effect on the nitrogen electronic surrounding of the named molecule, presumably through a hydrogen bridge bond between two of these atoms and the amino protons. For isopropylamine and aminoethanole wrong values of the coupling constants known in the literature could be corrected.

Introduction

Trifluoroethylamine, isopropylamine, and aminoethanole are three amino compounds with the amino groups placed in different chemical environments. Their schematic structure is shown in Figure 1. The ^{14}N-quadrupole coupling constants are sensitive indicators for changes of the nitrogen electronic surrounding caused by these different environments.

Trifluoroethylamine has the possibility to form intramolecular hydrogen bridge bonds between the highly electronegative fluorine atoms and the amino protons. We expect such an intramolecular interaction to have a strong impact on the nitrogen electronic structure. Aminoethanole can form a hydrogen bridge bond between the hydroxy proton and the nitrogen lone pair electrons. No possibility for any such interaction exists in the case of isopropylamine.

The microwave spectrum of trifluoroethylamine and the two deuterated species CF_3CH_2NHD and $CF_3CH_2ND_2$ was first measured and assigned by Warren and Wilson [1]. They found the spectrum of the trans-conformer and could not resolve the nitrogen hyperfine structure.

Mehrotra et al. observed the microwave spectrum of trans-isopropylamine and of the amino deuterated isotopomers for the first time [2]. They also determined ^{14}N-quadrupole coupling constants, but because the trace of their coupling tensor does not equal zero, they are completely unlikely.

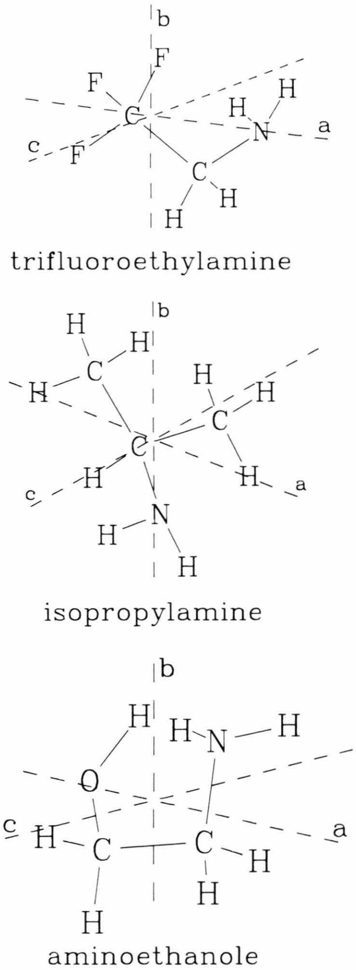

Fig. 1. Schematic structure of the amines. *a*, *b*, *c*: principal axes of inertia.

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Penn and Curl assigned the microwave spectrum of 6 isotopomers of aminoethanole and calculated a partial r_s-structure [3]. Some corrections of this structure were published later [4]. They determined the nitrogen quadrupole coupling constants from the hyperfine structure of two transitions. These coupling constants are not in accordance with the expected values for an amino group with the given orientation in the principal axis system.

It is for this reasons that a measurement respectively remeasurement of the quadrupole coupling constants of all three molecules including some isotopomers was reasonable.

Experimental

Trifluoroethylamine, isopropylamine and aminoethanole were purchased from Aldrich, Steinheim, in a purity of 99% and used without further purification. The dideuterated isotopomers $CF_3CH_2ND_2$ and $CH_3CHND_2CH_3$ were prepared by stirring the nondeuterated amine with five times the amount of D_2O for 24 hours, distilling the reaction product and repeating the whole procedure two more times.

The measurements were made with waveguide microwave Fourier transform (MWFT) spectrometers in the frequency range between 3.8 and 40 GHz [5–9] at pressures and temperatures given in the Tables 1–5 together with the listings of all measured transitions. One example is given in Figure 2. Because of low vapor pressure the measurement of aminoethanol was rather difficult. A two day conditioning period of the waveguide cell with the substance was necessary before any lines were detectable.

The Fourier transformation of a transient emission signal into the frequency domain causes line shape deformations, especially in the case of narrow multipletts [10]. To eliminate these overlap effects, the frequencies of the transitions were determined by a least squares fit of the time domain signal [11].

Results

Trifluoroethylamine

We measured 12 *a*-type transitions of trifluoroethylamine. Because this molecule is a near prolate top ($\varkappa = -0.98$), these transitions do not allow an accurate determination of the *A* rotational constant. It was therefore desirable to record *b*-type transitions in addition, but efforts to do this including the use of a molecular beam MWFT spectrometer described in [12] were unsuccessful.

We fitted the rotational and centrifugal distortion constants according to Watsons *A*-reduction in the I^r-representation to fourth order. The transitions from [1] were included in the fit. The quadrupole hyperfine structure was analysed using a first order perturbation calculation [13]. The same fit procedures were used for analysing the spectra of the other molecules published in this article.

We recorded 5 *a*-type transitions of trifluoroethylamine-d_2, sufficient to determine two quadrupole coupling constants. No splitting due to the deuterium quadrupole coupling was visible. The fit of the rotational constants was made with the centrifugal distortion constants fixed on the values of the nondeuterated isotopomer.

Isopropylamine

We recorded 15 *c*-type transitions of isopropylamine. The hyperfine structure of the $J \leftarrow J' = 2 \leftarrow 1$ transitions in the frequency range between 30 and 33 GHz contains valuable information about the quadrupole coupling. Their measurement was particularly useful for the accurate determination of the coupling constants.

The transitions with *J* quantum numbers higher than 8 were not included in the quadrupole fit. Because isopropylamine is a near oblate top ($\varkappa = 0.807$), the III^r-representation was chosen for the centrifugal distortion fit.

The amino group dideuteration of isopropylamine results in an exchange of the *a* and *b* principal inertia axes. 7 *c*-type transitions of isopropylamine-d_2 could be recorded. The deuterium quadrupole coupling was not resolvable but led to broadenings of the ^{14}N-hyperfine components. These broadenings did not allow us to resolve the rather narrow nitrogen hyperfine structure of the 3 measured Q-branch transitions. The rotational constants of isopropylamine-d_2 were fitted with the centrifugal distortion constants fixed on the values of isopropylamine, as described for trifluoroethylamine-d_2.

Aminoethanole

We measured 11 transitions of aminoethanole. Because it is not possible to fit all rotational and centri-

Table 1. Rotational transitions of trifluoroethylamine measured at a temperature of −50 °C and pressures of 0.1–0.35 Pa. ν_{obs}: measured frequency [MHz], $\Delta\nu_{hfs}$: hfs-splitting referred to the strongest component, δ_{hfs}: deviation of the experimental and the calculated splitting, ν_c: hypothetical unsplit line frequency calculated by adding the hfs-splittings to the frequencies of the components, δ_c: deviation of the centrifugal distortion calculation.

$J_{K_-K_+} \leftarrow J'_{K'_-K'_+}$	$F \leftarrow F'$	ν_{obs}	$\Delta\nu_{hfs}$	δ_{hfs}	ν_c	δ_c
$1_{01} \leftarrow 0_{00}$	2 ← 1	5 548.359				
	1 ← 1	5 547.944	0.415	−0.002	5 548.290	0.002
	0 ← 1	5 548.979	−0.621	0.002		
$2_{02} \leftarrow 1_{01}$	3 ← 2	11 096.436				
	1 ← 0	11 096.063	0.373	0.000	11 096.406	0.005
	2 ← 2	11 095.987	0.449	−0.003		
	1 ← 1	11 097.103	−0.667	0.005		
$2_{11} \leftarrow 1_{10}$	3 ← 2	11 119.764				
	2 ← 1	11 119.356	0.408	−0.001		
	1 ← 0	11 120.451	−0.687	0.001	11 119.701	0.005
	2 ← 2	11 119.841	−0.077	−0.002		
	1 ← 1	11 119.230	0.533	−0.002		
$2_{12} \leftarrow 1_{11}$	3 ← 2	11 073.511				
	2 ← 1	11 073.064	0.447	0.001		
	1 ← 0	11 073.693	−0.182	0.003	11 073.407	0.011
	2 ← 2	11 072.990	0.521	0.001		
	1 ← 1	11 073.883	−0.372	0.009		
$3_{21} \leftarrow 2_{20}$	4 ← 3	16 645.484				
	3 ← 2	16 645.049	0.436	0.002	16 645.391	0.019
	2 ← 1	16 645.728	−0.243	−0.001		
$3_{03} \leftarrow 2_{02}$	4 ← 3	16 644.197			16 644.179	0.008
	2 ← 1	16 644.113	0.084	0.000		
$3_{12} \leftarrow 2_{11}$	4 ← 3	16 679.448				
	3 ← 2	16 679.336	0.113	0.000	16 679.422	0.010
	2 ← 1	16 679.505	−0.056	0.001		
$3_{13} \leftarrow 2_{12}$	4 ← 3	16 610.033				
	3 ← 2	16 609.898	0.135	0.000	16 609.985	0.017
	2 ← 1	16 609.974	0.059	0.001		
	3 ← 3	16 609.376	0.657	0.000		
$3_{22} \leftarrow 2_{21}$	4 ← 3	16 644.849				
	3 ← 2	16 644.411	0.438	0.004	16 644.751	0.013
	2 ← 1	16 645.093	−0.244	−0.002		
$18_{1\,17} \leftarrow 18_{1\,18}$	19 ← 19	3 920.201				
	18 ← 18	3 920.867	−0.666	0.001	3 920.399	−0.002
	17 ← 17	3 920.165	0.036	0.001		
$19_{1\,18} \leftarrow 19_{1\,19}$	20 ← 20	4 346.043				
	19 ← 19	4 346.695	−0.652	−0.009	4 346.240	−0.002
	18 ← 18	4 346.003	0.040	−0.005		

Table 1 (continued)

$J_{K_-K_+} \leftarrow J'_{K'_-K'_+}$	$F \leftarrow F'$	ν_{obs}	$\Delta\nu_{hfs}$	δ_{hfs}	ν_c	δ_c
$20_{1\,19} \leftarrow 20_{1\,20}$	21 ← 21	4 791.017				
	20 ← 20	4 791.673	−0.656	−0.001	4 791.215	0.006
	19 ← 19	4 790.985	0.033	0.000		
$21_{1\,20} \leftarrow 21_{1\,21}$	22 ← 22	5 254.303				
	21 ← 21	5 254.956	−0.653	0.001	5 254.499	−0.001
	20 ← 20	5 254.267	0.036	−0.005		
$22_{1\,21} \leftarrow 22_{1\,22}$	23 ← 23	5 734.946				
	22 ← 22	5 735.594	−0.648	0.002	5 735.152	−0.001
	21 ← 21	5 734.914	0.322	−0.003		

Table 2. Rotational transitions of trifluoroethylamine-d$_2$ measured at a temperature of −50°C and pressures of 0.1–0.35 Pa. For explanations of symbols see Table 1.

$J_{K_-K_+} \leftarrow J'_{K'_-K'_+}$	$F \leftarrow F'$	ν_{obs}	$\Delta\nu_{hfs}$	δ_{hfs}	ν_c	δ_c
$1_{01} \leftarrow 0_{00}$	2 ← 1	5 246.610				
	1 ← 1	5 246.239	0.371	−0.001	5 246.548	
	0 ← 1	5 247.169	−0.559	0.004		
$2_{11} \leftarrow 1_{10}$	3 ← 2	10 503.513				
	2 ← 1	10 503.157	0.356	0.004		
	1 ← 0	10 504.185	−0.672	0.002	10 503.461	
	2 ← 2	10 503.647	−0.133	−0.004		
	1 ← 1	10 502.940	0.574	0.000		
$2_{12} \leftarrow 1_{11}$	3 ← 2	10 482.792				
	2 ← 1	10 482.389	0.403	0.002		
	1 ← 0	10 482.893	−0.101	−0.004	10 482.695	
	2 ← 2	10 482.257	0.535	−0.002		
	1 ← 1	10 483.214	−0.422	−0.003		
$3_{12} \leftarrow 2_{11}$	4 ← 3	15 755.166				
	3 ← 2	15 755.074	0.092	0.006	15 755.145	
	2 ← 1	15 755.228	−0.062	−0.000		
$3_{13} \leftarrow 2_{12}$	4 ← 3	15 724.041				
	3 ← 2	15 723.923	0.118	0.004	15 723.996	
	2 ← 1	15 723.972	0.069	−0.003		

Table 3. Rotational transitions of isopropylamine measured at temperatures between −30 and −50 °C and pressures of 0.2–0.6 Pa. For explanations of symbols see Table 1.

$J_{K_-K_+} \leftarrow J'_{K'_-K'_+}$	$F \leftarrow F'$	ν_{obs}	$\Delta\nu_{hfs}$	δ_{hfs}	ν_c	δ_c
$1_{10} \leftarrow 0_{00}$	2 ← 1	16 309.429				
	1 ← 1	16 308.121	1.308	−0.001	16 309.211	0.000
	0 ← 1	16 311.387	−1.958	−0.001		
$2_{11} \leftarrow 1_{01}$	3 ← 2	32 263.970				
	2 ← 1	32 262.607	1.362	−0.001		
	1 ← 0	32 265.231	−1.262	−0.001	32 263.697	0.000
	2 ← 2	32 263.147	0.823	0.002		
	1 ← 1	32 263.888	0.081	−0.003		
$2_{20} \leftarrow 1_{10}$	3 ← 2	32 645.250				
	2 ← 1	32 645.185	0.067	0.009		
	1 ← 0	32 644.062	1.188	0.004	32 645.161	0.000
	2 ← 2	32 643.871	1.379	0.002		
	1 ← 1	32 647.328	−2.078	0.004		
$2_{21} \leftarrow 1_{11}$	3 ← 2	32 973.151				
	2 ← 1	32 971.806	1.345	−0.001		
	1 ← 0	32 974.626	−1.475	0.001	32 972.895	−0.001
	2 ← 2	32 972.576	0.575	0.000		
	1 ← 1	32 972.699	0.452	−0.001		
$5_{51} \leftarrow 5_{41}$	6 ← 6	5 283.164				
	5 ← 5	5 283.430	−0.266	0.005	5 283.236	−0.000
	4 ← 4	5 283.116	0.048	0.005		
$6_{61} \leftarrow 6_{51}$	7 ← 7	7 340.614				
	6 ← 6	7 340.865	−0.250	−0.004	7 340.687	−0.009
	5 ← 5	7 340.575	0.039	0.004		
$7_{71} \leftarrow 7_{61}$	8 ← 8	9 668.934				
	7 ← 7	9 669.179	−0.245	0.003	9 669.005	0.001
	6 ← 6	9 668.902	0.032	0.003		
$8_{81} \leftarrow 8_{71}$	9 ← 9	12 210.026				
	8 ← 8	12 210.249	−0.223	−0.001	12 210.093	0.003
	7 ← 7	12 210.000	0.026	0.002		
$9_{82} \leftarrow 9_{72}$	10 ← 10	6 310.588				
	9 ← 9	6 310.812			6 310.654	0.015
	8 ← 8	6 310.557				
$13_{11\,3} \leftarrow 13_{10\,3}$	14 ← 14	6 541.416				
	13 ← 13	6 541.604			6 541.472	−0.001
	12 ← 12	6 541.394				
$17_{14\,4} \leftarrow 17_{13\,4}$	18 ← 18	6 259.730				
	16 ← 16				6 259.780	−0.009
	17 ← 17	6 259.884				

Table 3 (continued)

$J_{K_-K_+} \leftarrow J'_{K'_-K'_+}$	$F \leftarrow F'$	ν_{obs}	$\Delta\nu_{hfs}$	δ_{hfs}	ν_c	δ_c
$21_{17\,5} \leftarrow 21_{16\,5}$	22 ← 22	5 672.896				
	20 ← 20				5 672.936	0.007
	21 ← 21	5 673.022				
$22_{18\,5} \leftarrow 22_{17\,5}$	23 ← 23	7 936.402				
	21 ← 21				7 936.449	−0.033
	22 ← 22	7 936.547				
$26_{21\,6} \leftarrow 26_{20\,6}$	27 ← 27	7 021.987				
	25 ← 25				7 022.025	0.050
	26 ← 26	7 022.107				
$30_{24\,7} \leftarrow 30_{23\,7}$	31 ← 31	6 020.066				
	29 ← 29				6 020.097	−0.021
	30 ← 30	6 020.161				

Table 4. Rotational transitions of isopropylamine-d_2 measured at temperatures between −30 and −50 °C and pressures of 0.2–0.6 Pa. For explanations of symbols see Table 1.

$J_{K_-K_+} \leftarrow J'_{K'_-K'_+}$	$F \leftarrow F'$	ν_{obs}	$\Delta\nu_{hfs}$	δ_{hfs}	ν_c	δ_c
$1_{10} \leftarrow 0_{00}$	2 ← 1	15 296.954				
	1 ← 1	15 295.634	1.319	0.004	15 296.733	0.002
	0 ← 1	15 298.935	−1.981	−0.003		
$2_{11} \leftarrow 1_{01}$	3 ← 2	30 278.006				
	2 ← 1	30 276.642	1.364	−0.001		
	1 ← 0	30 279.485	−1.479	−0.004	30 277.746	0.001
	2 ← 2	30 277.410	0.596	−0.002		
	1 ← 1	30 277.570	0.436	0.002		
$2_{20} \leftarrow 1_{10}$	3 ← 2	30 615.883				
	2 ← 1	30 615.783	0.100	0.000		
	1 ← 0	30 614.693	1.190	0.004	30 615.787	−0.005
	2 ← 2	30 614.457	1.426	−0.002		
	1 ← 1	30 618.005	−2.122	0.008		
$2_{21} \leftarrow 1_{11}$	3 ← 2	30 909.213				
	2 ← 1	30 907.831	1.382	−0.004		
	1 ← 0	30 910.499	−1.286	−0.003	30 908.937	0.003
	2 ← 2	30 908.389	0.823	0.000		
	1 ← 1	30 909.120	0.093	0.004		
$5_{51} \leftarrow 5_{41}$					4 705.845	0.012
$6_{61} \leftarrow 6_{51}$					6 544.221	−0.009
$9_{91} \leftarrow 9_{81}$					13 354.234	0.001

Table 5. Rotational transitions of aminoethanole measured at temperatures between −30 and +20 °C and pressures of 0.1–2 Pa. For explanations of symbols see Table 1.

$J_{K_-K_+} \leftarrow J'_{K'_-K'_+}$	$F \leftarrow F'$	ν_{obs}	$\Delta\nu_{\mathrm{hfs}}$	δ_{hfs}	ν_{c}	δ_{c}
$1_{01} \leftarrow 0_{00}$	2 ← 1	10 116.977				
	1 ← 1	10 116.869	0.108	0.006	10 116.958	0.000
	0 ← 1	10 117.150	−0.173	0.001		
$2_{11} \leftarrow 2_{02}$	3 ← 3	10 989.503				
	2 ← 2	10 990.139	−0.636	0.010	10 989.642	−0.028
	1 ← 1	10 989.152	0.351	−0.004		
$3_{12} \leftarrow 3_{03}$	4 ← 4	12 702.997				
	3 ← 3	12 703.674	−0.678	−0.001	12 703.166	0.004
	2 ← 2	12 702.767	0.230	0.007		
$4_{13} \leftarrow 4_{14}$	5 ← 5	9 732.402				
	4 ← 4	9 733.473	−1.071	−0.008	9 732.690	0.035
	3 ← 3	9 732.125	0.277	0.000		
$7_{25} \leftarrow 7_{26}$	8 ← 8	7 973.115				
	7 ← 7	7 973.678	−0.562	0.001	7 973.279	−0.009
	6 ← 6	7 973.035	0.080	0.001		
$8_{26} \leftarrow 8_{27}$	9 ← 9	12 242.070				
	8 ← 8	12 242.706	−0.636	−0.002	12 242.259	0.018
	7 ← 7	12 241.990	0.080	0.000		
$9_{28} \leftarrow 9_{18}$	10 ← 10	10 436.018				
	9 ← 9	10 435.694	0.235	−0.009	10 435.924	−0.031
	8 ← 8	10 436.052	−0.033	−0.002		
$10_{29} \leftarrow 10_{19}$	11 ← 11	7 910.878				
	10 ← 10	7 910.625	0.253	0.001	7 910.801	0.034
	9 ← 9	7 910.900	−0.022	−0.004		
$11_{38} \leftarrow 11_{39}$	12 ← 12	8 509.464				
	11 ← 11	8 509.842	−0.378	0.002	8 509.580	−0.010
	10 ← 10	8 509.433	0.031	0.003		
$15_{4\,11} \leftarrow 15_{4\,12}$	16 ← 16	8 144.173				
	15 ← 15	8 144.440	−0.267	0.000	8 144.257	−0.014
	14 ← 14	8 144.153	0.020	−0.002		
$16_{4\,12} \leftarrow 16_{4\,13}$	17 ← 17	12 300.168				
	16 ← 16	12 300.508	−0.340	0.006	12 300.273	0.002
	15 ← 15	12 300.153	0.015	0.006		

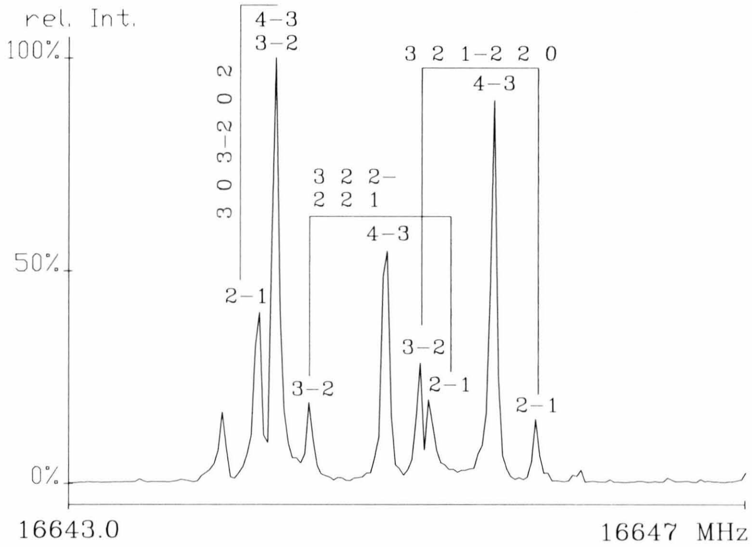

Fig. 2. Power spectrum of three rotational transitions of trifluoroethylamine labeled by $J\,K_-\,K_+$ and F quantum numbers, polarization frequency 16 646 MHz, 4800 k averaging cycles, sample interval 10 ns, 4096 data points, pressure 0.07 Pa, temperature −45 °C.

Table 6. Rotational and centrifugal distortion constants. A, B, C: rotational constants [MHz], Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K: fourth order centrifugal distortion constants according to Watsons A-reduction [kHz], $\varkappa$: asymmetry parameter, σ: standard deviation of the fit [kHz], standard errors in brackets.

	trifluoroethylamine	trifluoroethylamine-d$_2$	isopropylamine	isopropylamine-d$_2$	aminoethanole
representation	I^r	I^r	III^r	III^r	I^r
A	5308(14)	5216(39)	8831.921(21)	7806.170(11)	14508.72(15)
B	2785.722(3)	2628.714(2)	7977.320(21)	7490.594(11)	5546.48(12)
C	2762.578(3)	2617.842(2)	4657.170(76)	4331.793(38)	4570.47(12)
Δ_J	0.560(45)		7.4(22)		-1.2(71)
Δ_{JK}	1.99(66)		-12.94(53)		-26.89(36)
Δ_K	26480(470)		-9.6(52)		96.8(54)
δ_J	0.0033(39)		0.1443(83)		1.738(12)
δ_K	124(36)		-6.43(72)		13.63(36)
κ	-0.9814	-0.9916	0.8070	0.8183	-0.8036
σ	31	26	25	8	29

Table 7. Quadrupole coupling constants [MHz] in the principal inertia axis system. $\Delta\bar{\nu}_{exp}$: mean experimental hfs-splitting [MHz], σ: standard deviation of the fit [kHz], standard errors in brackets.

	trifluoroethylamine	trifluoroethylamine-d$_2$	isopropylamine	isopropylamine-d$_2$	aminoethanole
χ_{aa}	-1.375(3)	-1.232(4)	1.789(2)	2.563(5)	-0.382(11)
χ_{bb}	-0.261(3)	-0.427(7)	2.566(4)	1.850(7)	-1.404(11)
χ_{cc}	1.636(3)	1.659(7)	-4.355(4)	-4.413(7)	1.786(11)
$\Delta\bar{\nu}_{exp}$	0.354	0.319	0.749	1.114	0.298
σ	3	3	3	4	5

fugal distortion constants to 11 transitions simultaneously, separate calculations were made to fit the rotational and centrifugal distortion constants. Although this proceeding entails some ambiguities and the result must be regarded with care, the constants obtained this way do reproduce the observed spectrum.

The rotational and centrifugal distortion constants of all molecules are summarized in Table 6. The quadrupole coupling constants in the principal inertia axis system are given in Table 7. For isopropylamine, isopropylamine-d$_2$, and aminoethanole they are completely different from the coupling constants given in [2] and [3]. That means the values given in these two publications are incorrect.

For direct comparisons of quadrupole coupling constants of different nitrogen containing molecules it is necessary to transform the coupling tensor in its own principal axis system. Since no spectral lines in the range of our spectrometers are sensitive to non-diagonal elements, this task can only be accomplished by the measurement of the coupling constants of an isotopomer and then following a procedure given in an article written by Zeil [14]. This approach works in a simple way only on condition that both the normal and the isotopic substituted molecule have a molecular plane of symmetry and that the isotopic substitution rotates the principal inertia axis system a sufficient angle about the axis perpendicular to that plane to have a measurable effect on the coupling constants in the principal inertia axis system. It is assumed that the isotopic substitution does not change the nitrogen electronic surrounding.

Trifluoroethylamine and isopropylamine possess such a plane of symmetry, which has the same orientation with respect to the amino group for both molecules. The rotational angle caused by the substitution can be calculated directly from the rotational con-

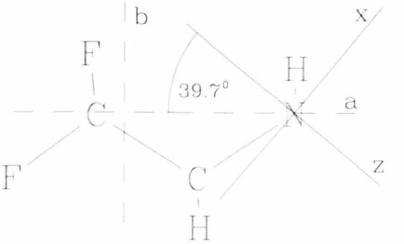

Fig. 3. Trifluoroethylamine with its principal axes of inertia (*a*, *b*) and of the quadrupole coupling tensor (*x*, *z*).

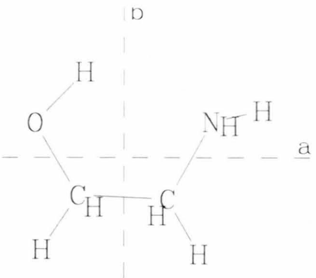

Fig. 4. Aminoethanole in a projection on the *a*, *b*-principal inertia axis plane. The dotted line indicates the expected direction of the nitrogen line electron pair.

Table 8. Principal quadrupole coupling constants [MHz]. ϑ: rotational angle of the principal inertia axis system caused by the isotopic substitution (see text), θ_{za}: angle between the *a*-principal inertia axis and the *z*-principal coupling tensor axis.

	trifluoroethylamine	ethylamine [16]
ϑ	1.37(22)°	
θ_{za}	39.7(8)°	
χ_{xx}	2.21(40)	2.9(2)
χ_{yy}	1.636(3)	1.755(6)
χ_{zz}	-3.85(40)	-4.7(2)

Table 9. Coupling constants χ_{yy} [MHz] of different amines with a symmetry plane oriented in the same way with respect to the amino group. Values of ethylamine and cyclopropylamine taken from [16] and [17] respectively.

isopropylamine	1.789(2)
isopropylamine-d_2	1.850(7)
ethylamine	1.755(60)
ethylamine-d_2	1.850(60)
cyclopropylamine	1.787(2)
trifluoroethylamine	1.636(3)
trifluoroethylamine-d_2	1.659(7)

stants of both isotopomers [15]. This angle is 1.37(22)° for the amino dideuteration of trifluoroethylamine but only 0.49(1)° for the amino dideuteration of isopropylamine. While an angle of 1.37(22)° entails rather a great error margin in the calculation of the coupling tensor in its principal axis system, an angle of only 0.49(1)° does not even allow to perform a useful calculation. The coupling constants χ_{xx}, χ_{yy}, χ_{zz} (*x*, *y*, *z*: principal axis system of the coupling tensor) of trifluoroethylamine are given in Table 8. The orientation of the coupling tensor is shown in Figure 3. For the given reason no such calculation was possible for isopropylamine. Because aminoethanole does not possess a molecular plane of symmetry the method of [14] is not applicable.

Discussion

Only in the case of trifluoroethylamine we succeeded in determining the *complete* nitrogen quadrupole coupling tensor. To study the effects the fluorine atoms have on the nitrogen electronic structure, we compare the results with the coupling constants of ethylamine [16]. The constants of both molecules are presented in Table 8 for direct comparison. The only difference in the composition of the molecules are the fluorine atoms. They must therefore cause the change of the coupling constants. All coupling constants are lower for trifluoroethylamine. The lower value of χ_{zz} indicates a decrease in the lone pair electron density. This allows to draw the conclusion that there is in fact a kind of hydrogen bridge bond between the fluorine atoms and the amino protons.

Because the symmetry plane of isopropylamine entails that one principal inertia axis coincides with one principal coupling axis, we know the principal coupling constant belonging to this axis, which we identify with the *y*-axis. Cyclopropylamine and the just mentioned ethylamine are two more amines with a molecular plane of symmetry oriented in the same way with respect to the amino group as in trifluoroethylamine and isopropylamine. Their coupling constants are known [17, 16]. The values of χ_{yy} of all these molecules are summarized in Table 9. One can draw some conclusions from this Table.

The dideuteration of the amino group causes a slight increase of χ_{yy}, which is smaller but still measurable in the case of trifluoroethylamine. That means the isotopic substitution does change the nitrogen electronic surrounding a bit and introduces an error in the principal coupling constants determined by the method of Zeil [14] independent of other possible sources of error.

As mentioned earlier, an interaction with the fluorine atoms causes χ_{yy} to decrease for trifluoroethylamine compared to all other amines, for which the values of χ_{yy} are nearly identical if one looks at the nondeuterated respectively deuterated isotopomers.

No principal coupling constant of aminoethanole is known. Figure 4 shows this molecule in the projection on the *ab*-principal inertia axis plane. The dotted line indicates the expected direction of the nitrogen lone electron pair, which can be identified with the *z*-axis of the coupling tensor principal axis system. Taking χ_{zz} and χ_{xx} from ethylamine and neglecting that the N-atom is out off the *ab*-plane one can make the rough estimation that χ_{bb} should be negative. That is in accordance with our coupling constants from Table 7, but in contradiction to the values of Penn and Curl [3], which are based on a misassignment of hyperfine components. This misassignment can be recognized by comparing the hyperfine component frequencies of the transition $1_{01} \leftarrow 0_{00}$ in Table VII of [3] and Table 5 of this paper.

Microwave Fourier transform spectroscopy has now proved to be a useful tool for investigation of the electronic structure not only of planar nitrogen containing molecules but also of amines which contain nitrogen with a nonplanar sp_3-hybridization.

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