^{14}N Quadrupole Coupling in the Rotational Spectrum of Ethyl Nitrite

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We investigated the ^{14}N quadrupole coupling of three rotational isomers of ethyl nitrite in the ground state by microwave Fourier transform spectroscopy. Centrifugal distortion analyses were necessary to assign the transitions with high J quantum numbers. We found an additional splitting of some c-type transitions of the trans-gauche rotamer presumably arising from tunneling through the barrier separating the two equivalent gauche forms. This assumption could not be confirmed yet.

Introduction

The microwave spectrum of ethyl nitrite, CH_3CH_2ONO, in the vibrational ground and some excited torsional states was first investigated and assigned by Turner [1]. He found the existence of three rotational isomers called cis-trans, cis-gauche, and trans-gauche ethyl nitrite, which are shown in Figure 1. He observed μ_a and μ_b transitions of the cis-trans, μ_a transitions of the cis-gauche, and μ_a and μ_c transitions of the trans-gauche rotamer. Later Endo et al. [2] recorded the microwave spectra of D_5-ethyl nitrite and the ^{15}N isotope of ethyl nitrite. They used the results to calculate a partial r_0 structure.

By use of a conventional Stark spectrometer Turner resolved only parts of the nitrogen hyperfine structure in a few transitions. It was our aim to use the advantages of microwave Fourier transform (MWFT) spectroscopy, especially the much higher resolution, to determine the quadrupole coupling constants of the three rotational isomers in the ground state.

Experimental

Ethyl nitrite was purchased from Fa. Merck-Schuchardt, Darmstadt, in a purity of 85% and distilled under low pressure for further purification. The spectra were taken with our MWFT spectrometers [3 – 7] in the range of 5 to 36 GHz at pressures between 0.025 and 0.2 Pa (0.2 – 1.5 mTorr) and at temperatures between −30 and −55 °C. The Fourier transformation of a transient emission signal into the frequency domain leads to line shape deformations, especially in the case of narrow multiplets [8]. To avoid these effects, the time domain signals were analysed using a computer program to obtain the frequencies, amplitudes, phases, and line widths contained in the signals [9]. Lists of some measurements are given in the Tables 1, 2, and 3. The complete list of measurements is available under number TNA 16 from the Universitätsbibliothek, Westring 400, D-2300 Kiel.

The observed splittings arising from nitrogen quadrupole coupling were used for a first order hfs analysis [10]. Some c-type transitions of the trans-gauche rotamer show an additional splitting of each ^{14}N-hfs component into two lines. The mean value of the two

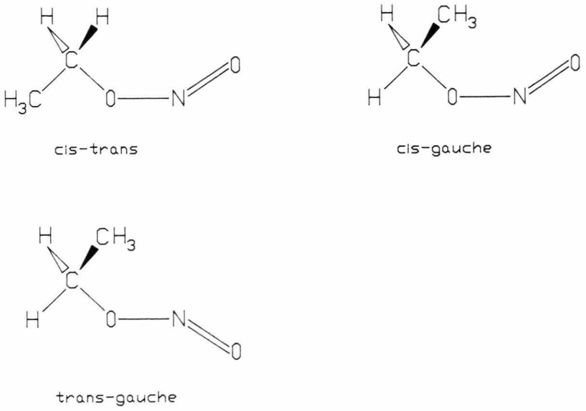

Fig. 1. Rotational isomers of ethyl nitrite.

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Table 1. Measured line frequencies of cis-trans ethyl nitrite with hfs-splittings. ν: measured frequency, $\Delta\nu_{\text{hfs}}$: hfs-splitting referred to the strongest component, δ_{hfs}: deviation of the experimental and the calculated splitting, ν_0: hypothetical unsplit line frequency calculated by adding the hfs-splittings to the frequencies of the components, δ_0: deviation of the centrifugal distortion calculation.

J	K_-	K_+	$-$	J'	K'_-	K'_+	$F-F'$	ν [MHz]	$\Delta\nu_{\text{hfs}}$ [MHz]	δ_{hfs} [kHz]	ν_0 [MHz]	δ_0 [kHz]
3	2	1	−	2	2	0	4−3	17107.220			17107.321	2
							3−2	17107.669	−0.449	2		
							2−1	17106.997	0.224	9		
4	0	4	−	3	0	3	5−4	22719.370			22719.361	−2
							4−3	22719.309	0.061	−6		
							3−2	22719.417	−0.046	1		
4	1	3	−	4	0	4	5−5	16972.590			16972.974	5
							4−4	16974.027	−1.437	0		
							3−3	16972.213	0.377	−8		
5	0	5	−	4	1	4	6−5	14835.241			14835.578	−6
							5−4	14836.498	−1.257	2		
							4−3	14834.934	0.307	5		
6	1	5	−	6	0	6	7−7	19118.437			19118.905	−1
							6−6	19120.072	−1.635	−2		
							5−5	19118.157	0.280	−4		
6	0	6	−	5	1	5	7−6	21213.677			21214.005	5
							6−5	21214.852	−1.175	−1		
							5−4	21213.436	0.241	−5		
8	1	7	−	8	0	8	9−9	22307.019			22307.563	−7
							8−8	22308.859	−1.840	3		
							7−7	22306.776	0.243	−11		
17	2	15	−	17	2	16	18−18	18048.558			18049.087	0
							17−17	18050.222	−1.664			
							16−16	18048.443	0.115			

Table 2. Measured line frequencies of cis-gauche ethyl nitrite with hfs-splittings. Explanations of symbols see Table 1

J	K_-	K_+	$-$	J'	K'_-	K'_+	$F-F'$	ν [MHz]	$\Delta\nu_{\text{hfs}}$ [MHz]	δ_{hfs} [kHz]	ν_0 [MHz]	δ_0 [kHz]
2	0	2	−	1	0	1	3−2	14559.643			14559.629	−17
							2−1	14559.613	0.031	−1		
3	2	1	−	2	2	0	4−3	22107.292			22107.271	2
							3−2	22107.193	0.099	2		
							2−1	22107.359	−0.067	0		
3	1	2	−	2	1	1	4−3	22862.142			22862.137	−9
							3−2	22862.094	0.048	−11		
							2−1	22862.187	−0.045	1		
3	1	3	−	2	1	2	4−3	20901.977			20901.956	−2
							3−2 2−1	20901.924	0.053	−6		
3	2	2	−	2	2	1	4−3	21913.204			21913.172	2
							3−2	21913.065	0.139	−4		
							2−1	21913.275	−0.072	−3		
4	1	3	−	4	1	4	5−5	6525.287			6525.410	−1
							4−4	6525.742	−0.455	−5		
							3−3	6525.160	0.127	−9		
7	2	5	−	7	2	6	8−8	5221.121			5221.189	−2
							7−7	5221.355	−0.234	2		
							6−6	5221.078	0.043	−10		

Table 3. Measured line frequencies of trans-gauche ethyl nitrite with hfs-splittings. Explanations of symbols see Table 1. ν_{hc}: mean value of two frequencies belonging to a doublet arising from the additional splitting discussed in the text.

J	K_-	K_+	$-\ J'$	K'_-	K'_+	$F-F'$	ν [MHz]	ν_{hc} [MHz]	$\Delta\nu_{\text{hfs}}$ [MHz]	δ_{hfs} [kHz]	ν_0 [MHz]	δ_0 [kHz]
3	2	1	– 2	2	0	4– 3	16103.018				16103.057	5
						3– 2	16103.203		–0.184	7		
						2– 1	16102.297		0.091	12		
3	2	2	– 2	2	1	4– 3	16099.808				16099.850	–2
						3– 2	16100.004		–0.197	6		
						2– 1	16099.174		0.094	12		
4	1	4	– 3	1	3	5– 4	21208.315				21208.350	16
						4– 3	21208.366		–0.051	–2		
						3– 2	21208.413		–0.099	–3		
4	1	4	– 4	0	4	5– 5	14333.091				14333.372	19
						4– 4	14334.137		–1.046	–7		
						3– 3	14332.819		0.277	0		
5	1	5	– 4	1	4	6– 5	26508.382				26508.407	13
						5– 4 4– 3	26508.446		–0.064	2		
7	1	7	– 7	0	7	8– 8	13267.148 13267.200	13267.174			13267.479	23
						7– 7	13268.195 13268.245	13268.220	–1.046	2		
						6– 6	13266.995 13267.047	13267.020	0.154	–3		
7	0	7	– 6	1	5	8– 7	21176.426 21176.492	21176.459			21176.826	2
						7– 6	21177.694 21177.777	21177.736	–1.277	0		
						6– 5	21176.219 21176.287	21176.253	0.206	1		
8	1	8	– 8	0	8	9– 9	12815.221 12815.276	12815.249			12815.553	18
						8– 8	12816.241 12816.302	12816.272	–1.023	–1		
						7– 7	12815.092 12815.146	12815.119	0.130	–1		
9	1	9	– 9	0	9	10–10	12322.685 12322.737	12322.711			12323.011	13
						9– 9	12323.680 12323.742	12323.711	–1.000	3		
						8– 8	12322.578 12322.638	12322.608	0.103	8		
10	1	10	–10	0	10	11–11	11794.981 11794.930	11794.956			11795.252	4
						10–10	11795.898 11795.952	11795.925	–0.969	3		
						9– 9	11794.828 11794.869	11794.849	0.107	–10		
25	2	24	–25	1	24	26–26 24–24	26697.196 26697.333	26697.265			26697.571	15
						25–25	26698.201 26698.316	26698.259	–0.994			
26	2	25	–26	1	25	27–27 25–25	25479.598 25479.725	25479.662			25479.960	16
						26–26	25480.573 25480.689	25480.631	–0.969			

Table 3 (continued)

J	K_-	K_+	$-$ J'	K'_-	K'_+	$F-F'$	ν [MHz]	ν_{hc} [MHz]	$\Delta\nu_{\mathrm{hfs}}$ [MHz]	δ_{hfs} [kHz]	ν_0 [MHz]	δ_0 [kHz]
31	2	30	−31	1	30	32−32 30−30	19424.125 19424.265	19424.195			19424.445	−6
						31−31	19424.939 19424.265	19425.009	−0.814			
32	2	31	−31	1	31	33−33 31−31	18256.756 18256.904	18256.830			18257.063	−4
						32−32	18257.532 18257.681	18257.607	−0.777			

Table 4. Quadrupole coupling constants [MHz] of ethyl nitrite, χ^+, χ^-: quadrupole coupling constants, $|(\chi^+, \chi^-)|$: correlation coefficient, $\Delta\bar{\nu}_{\mathrm{exp}}$: mean experimental hfs-splitting [MHz], σ: standard deviation [MHz] of the fit, standard errors in brackets.

	cis-trans	cis-gauche	trans-gauche
$\chi^+ = \chi_{bb} + \chi_{cc}$	−1.243 (10)	0.418 (9)	−0.595 (12)
$\chi^- = \chi_{bb} - \chi_{cc}$	−8.119 (12)	−1.359 (17)	6.565 (15)
χ_{aa}	1.243 (10)	−0.418 (9)	0.595 (12)
χ_{bb}	−4.681 (11)	−0.471 (13)	2.985 (14)
χ_{cc}	3.438 (11)	0.888 (13)	−3.580 (14)
$|(\chi^+, \chi^-)|$	0.100	−0.036	−0.060
$\Delta\bar{\nu}_{\mathrm{exp}}$	0.879	0.119	0.427
σ	0.008	0.007	0.006

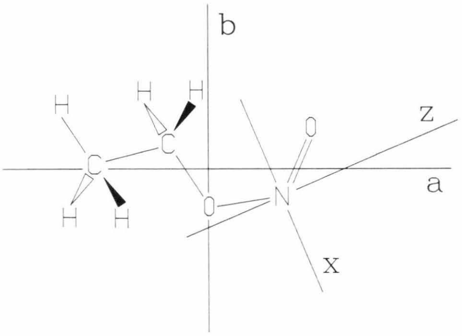

Fig. 2. Cis-trans ethyl nitrite with its principal axes of inertia (a, b) and of the quadrupole coupling tensor (x, z). Structure taken from [2], coupling tensor axis directions taken from cis methyl nitrite [13].

frequencies belonging to one ^{14}N-hfs component was used for the hfs analysis. This splitting will be discussed later. Because centrifugal distortion has remarkable effects on nitrogen quadrupole coupling in the transitions with angular momentum quantum numbers J higher than 10, these transitions were excluded from the hfs analysis. The inclusion of those lines in these fits results in increasing standard errors of the coupling constants. We give the results in the Table 4. In the next step of the analysis, the coupling constants were used to calculate the splittings relative to a single rigid rotor line and to correct the experimental hfs components with these splittings to obtain hypothetical unsplit line frequencies ν_0. We used the unsplit line frequencies to carry out a centrifugal distortion analysis based on the Hamiltonian according to Watsons S-reduction [11]. The lines measured by Turner [1] were included in the fits. Fourth order analyses were sufficient for the cis-trans and cis-gauche rotamer. A sixth order analysis had to be performed to achieve a good agreement between the calculated and observed spectrum of the trans-gauche conformer. Because it was not possible to fit the constants h_1, h_2, h_3, they were fixed to a value of zero. The rotational and centrifugal distortion constants are given in the Table 5.

Discussion

We measured the diagonal elements of the quadrupole coupling tensor in the principal axes of inertia. Within the range of the MWFT spectrometer no splitting is sensitive to non diagonal elements. Therefore it is not possible to perform a direct diagonalization of the coupling tensor. Another possibility to gain the tensor in its principal axis system is to determine the quadrupole coupling constants of another isotopically substituted species of the same conformer. This substitution leads to a rotation of the principal axis system of inertia, and one can diagonalize the coupling tensor following the procedure given in [12].

Table 5. Rotational and centrifugal distortion constants of ethyl nitrite, A, B, C; rotational constants, D_J, D_{JK}, D_K, d_1, d_2: fourth order centrifugal distortion constants according to Watsons S-reduction, H_J, H_{JK}, H_{KJ}, H_K: sixth order centrifugal distortion constants according to Watsons S-reduction, $\varkappa$: asymmetry parameter, σ: standard deviation of the fit, standard errors in brackets.

Cis-trans ethyl nitrite

			Correlation matrix							
A	18019.929(45)	MHz	1							
B	3019.9878(70)	MHz	0.370	1						
C	2674.6066(64)	MHz	0.261	0.604	1					
D_J	0.698(11)	kHz	0.162	0.878	0.696	1				
D_{JK}	−1.99(10)	kHz	0.622	0.259	0.387	0.035	1			
D_K	−830.1(49)	kHz	0.484	0.265	−0.216	0.188	−0.140	1		
d_1	−0.0969(19)	kHz	0.147	−0.391	0.436	−0.224	0.367	−0.317	1	
d_2	0.0122(11)	kHz	−0.371	0.254	−0.456	0.164	−0.547	0.136	−0.960	1
$\varkappa$	−0.9550									
σ	0.006	MHz								

Cis-gauche ethyl nitrite

			Correlation matrix							
A	10139.30(10)	MHz	1							
B	3979.3277(17)	MHz	−0.252	1						
C	3325.0525(16)	MHz	−0.390	0.022	1					
D_J	5.104(36)	kHz	0.634	0.010	0.289	1				
D_{JK}	−24.24(54)	kHz	−0.865	0.469	0.311	−0.661	1			
D_K	0.016(25)	MHz	−0.756	0.575	−0.023	−0.695	0.810	1		
d_1	−1.629(21)	kHz	0.012	−0.655	0.611	0.196	−0.130	−0.442	1	
d_2	−0.025(24)	kHz	0.912	−0.303	−0.364	0.679	−0.904	−0.853	−0.057	1
æ	−0.8095									
σ	0.011	MHz								

Trans gauche ethyl nitrite

			Correlation matrix											
A	17639.448(11)	MHz	1											
B	2746.3989(7)	MHz	0.486	1										
C	2619.5175(9)	MHz	−0.285	0.609	1									
D_J	4.301(11)	kHz	−0.296	0.397	0.729	1								
D_{JK}	−106.55(11)	kHz	−0.061	−0.253	−0.156	−0.696	1							
D_K	1.2862(47)	MHz	0.005	0.410	0.454	0.887	−0.931	1						
d_1	−1.215(1)	kHz	−0.405	0.154	0.639	0.845	−0.638	0.772	1					
d_2	−0.05928(36)	kHz	0.251	−0.271	−0.667	−0.646	0.326	−0.533	−0.853	1				
H_J	0.0002727(62)	kHz	−0.750	−0.212	0.463	0.332	0.238	−0.083	0.370	−0.301	1			
H_{JK}	0.00905(13)	kHz	−0.452	0.107	0.660	0.799	−0.537	0.687	0.989	−0.853	0.449	1		
H_{KJ}	−0.0445(45)	kHz	−0.188	−0.389	−0.307	−0.676	0.892	−0.912	−0.684	0.526	0.390	−0.599	1	
H_K	0.349(80)	kHz	0.103	0.415	0.392	0.800	−0.929	0.978	0.740	−0.539	−0.246	0.652	−0.978	1
$\varkappa$	−0.9831													
σ	0.021	MHz												

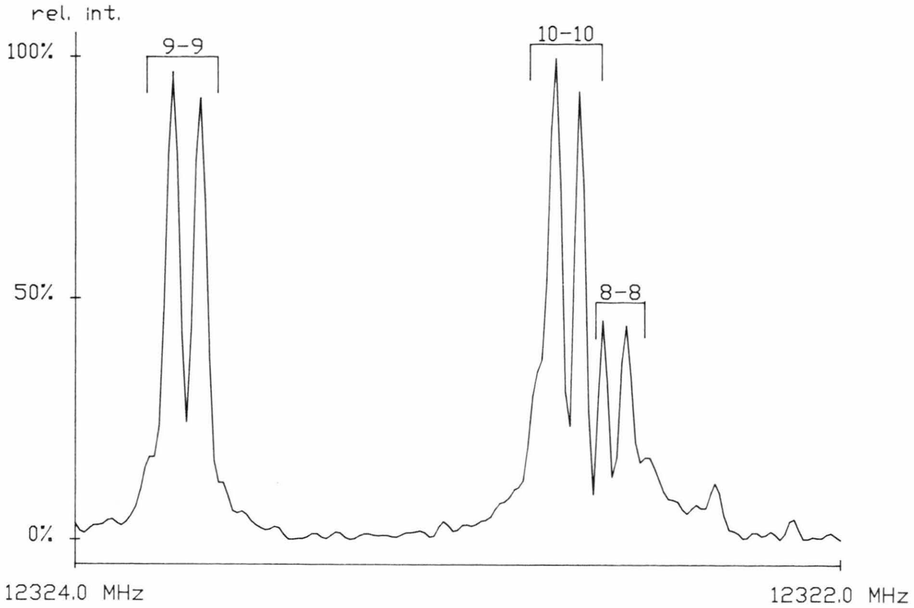

Fig. 3. Nitrogen hfs and additional splitting of the transition $9_{19}-9_{09}$, power spectrum, polarization frequency: 12320.996 MHz, sample interval 20 ns, $4.9 \cdot 10^6$ averaging cycles, 1024 data points supplemented with 3096 zeros, pressure: 0.6 mTorr, temperature: $-50\,^\circ$C.

Table 6. Coupling constants in the principal axis system of the coupling tensor.

Cis-trans ethyl nitrite		Cis methyl nitrite [13]	
χ_{xx}	-6.09 MHz	χ_{xx}	$-5.9\ (5)$ MHz
χ_{yy}	3.44 MHz	χ_{yy}	3.47(3) MHz
χ_{zz}	2.65 MHz	χ_{zz}	2.4 (5) MHz

Because the replacement of all hydrogen by deuterium atoms rotates the principal axis system of inertia only by about 0.4°, this method does not work in the case of ethyl nitrite. A rotation angle of at least 3° is necessary for a successful application of the method.

In the case of cis-trans ethyl nitrite there is another possibility to try a diagonalization of the coupling tensor. The structure of cis methyl nitrite and the ^{14}N-quadrupole coupling constants in the principal axis system of the coupling tensor have been determined by Turner [13] et al. According to [2] and [13], the structures of the CONO-group in cis-trans ethyl nitrite and cis methyl nitrite are identical with an *ab*-plane of symmetry. We assume that the principal axes of the coupling tensor have the same direction in both molecules. This assumption is based on the fact that the values of $\chi_{cc} = \chi_{yy} = 3.438\,(11)$ MHz obtained for cis-trans nitrite in this work and $\chi_{cc} = \chi_{yy} = 3.47(3)$ MHz obtained for cis methyl nitrite [13] are identical within their standard errors. We apply the formulas given in [14] to transform the coupling tensor of cis-trans ethyl nitrite from the principal axis system of inertia in the principal axis system of the coupling tensor taken from cis methyl nitrite. Because our results are based on an assumption we present them in Table 6 without errors. A comparison with the results for cis methyl nitrite from [13], also given in Table 6, leads to the conclusion that in fact the principal axis directions of the coupling tensor are the same or at least nearly the same in both molecules. Because cis-trans ethyl nitrite merely differs from cis methyl nitrite by a methyl group no other result is expected. The rotamer with its principal axes of inertia and of the coupling tensor is shown in Figure 2. Because of the lack of comparable molecules similar considerations are not possible for the other two ethyl nitrite rotamers.

Another aspect to discuss is the additional splitting of each ^{14}N-hfs component into a doublet in some *c*-type transitions of trans-gauche ethyl nitrite. An example is shown in Fig. 3. No final interpretation of this splitting has been achieved up to now. We failed in an attempt to fit it to a methyl group internal rotation with a program using the Hamiltonian according to Woods IAM-theory [15]. The splitting seems to arise from the tunneling between the two equivalent trans-gauche rotamers. Further work must be done to confirm this hypothesis.

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