Deuterium Hyperfine Structure of Nitric Acid – ^{15}N

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In this paper we present the determination of the deuterium quadrupole tensor of nitric acid $D^{15}NO_3$, performed with microwave Fourier transform spectroscopy applied to a gas sample in thermodynamic equilibrium. Hitherto molecular beam methods had to be used for similar investigations.

In the course of our efforts to investigate fine structures of rotational spectra by application of microwave Fourier transform (MWFT) spectroscopy [1–3] we succeeded in resolving the deuterium hyperfine structure (D-hfs) of nitric acid. To minimize complications we selected the isotopic species $D^{15}NO_3$. Our work is based on the assignment and results given by Cox et al. [4]. For the precalculation of the hfs-pattern it proved useful to transfer the data from formic acid, HCOOD [5]. The determination of the structure by [4] was of great help.

The sample was prepared by reaction of potassium nitrate-^{15}N ($K^{15}NO_3$) with deuterosulfuric acid (D_2SO_4), 90% deuterated and purchased from Fa. Merck, and used after distillation.

In Table 1 we give the measured lines under ν_{exp}. Figure 1 shows an example. As we recently noticed that the value $\Delta\nu$ in closely split lines shows a systematic error, we simulated the patterns by numerically producing a transient decay. Frequency, amplitude, line width and phase of the decay can be adjusted. A comparison with the experiment is made after Fourier transformation. Thereupon the input data are modified in such a way to achieve a better agreement with the measured multiplet. The result of this simulation is given under ν_{sim}. We take these frequencies as basis of our analysis.

For a check of the assignment a centrifugal distortion analysis was made with Watson's s-reduction [6–8]. As the molecule is planar [4], the planarity constraint was introduced. Because of the small number of lines this is not a final result. To make possible a comparison with the centrifugal distortion constants for the normal species, HNO_3, as given in [9], we also performed an analysis with Watson's a-reduction [6]. The values roughly agree with those of Table II of [9].

For the hfs-analysis first order theory was used. There is no line sensitive enough to χ_{ab} in the measuring range of our spectrometer. The results (χ_+ and χ_-) are given in Table 2, together with the

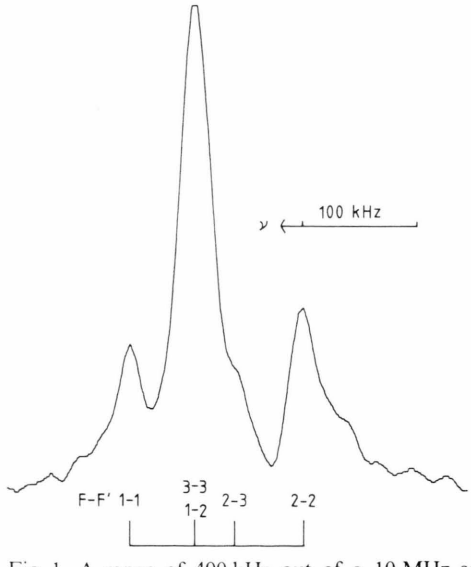

Fig. 1. A range of 400 kHz out of a 10 MHz scan of the rotational spectrum of $D^{15}NO_3$. – Rotational transition: $2_{11}-2_{12}$; power spectrum, sample interval: 50 ns, 1280 K cycles, 1024 data points supplemented by 3072 zeros, microwave polarizing frequency: $\nu_{MW} = 15822$ MHz; pressure: $p = 0.07$ mTorr, temperature: $T = -63$ °C.

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Table 1. Measured transitions of $D^{15}NO_3$. ν_{exp}: experimental frequency, ν_{sim}: corrected frequency, ν_0: unsplit frequency, *: not used for quadrupole hfs analysis, nr: not resolved; frequencies, splittings and deviations in MHz.

J	K_-	K_+	–	J'	K'_-	K'_+	$F - F'$	ν_{exp}	ν_{sim}	ν_0	$\nu_{sim} - \nu_0$	$\delta_{calc-exp}$
1	0	1	–	0	0	0		17 342.448		17 342.448	nr	
1	1	0	–	1	0	1	2 – 2 2 – 1	6 937.702	6 937.703	6 937.696	0.007	0.002
							1 – 1		6 937.674		– 0.022	– 0.003
							1 – 2	6 937.653	6 937.658		– 0.038	0.004
							0 – 1	6 937.777	6 937.777		0.081	– 0.009
							1 – 0	6 937.636	6 937.642		– 0.054	0.007
1	1	0	–	1	1	1	2 – 2 0 – 1	5 274.451	5 274.452	5 274.437	0.015	0.002
							1 – 1	5 274.360	5 274.364		– 0.073	0.001
							2 – 1 1 – 2	5 274.405	5 274.409		– 0.028	– 0.001
							1 – 0	5 274.483	5 274.484		0.047	0.000
2	1	1	–	2	1	2	3 – 3 1 – 2	15 823.188	15 823.189	15 823.172	0.017	0.002
							2 – 2	15 823.094	15 823.102		– 0.070	– 0.002
							1 – 1	15 823.244	15 823.243		0.071	0.001
							2 – 3		15 823.154		– 0.018 *	– 0.013
2	2	0	–	2	1	1		8 936.076		8 936.076	nr	
3	3	0	–	3	2	1		12 455.251		12 455.251	nr	
4	3	1	–	4	3	2	5 – 5 3 – 3	10 785.554	10 785.554	10 785.543	0.011	0.005
							4 – 4	10 785.509	10 785.516		– 0.027	– 0.006
5	4	1	–	5	4	2	6 – 6 4 – 4	7 807.137	7 807.138	7 807.131	0.007	0.005
							5 – 5	7 807.109	7 807.112		– 0.019	– 0.005

Table 2. Rotational [MHz], centrifugal distortion [kHz] and deuterium-hfs [MHz] constants of nitric acid-D, ^{15}N. N: number of lines, $|(a, b)|$: correlation, σ: standard deviation [kHz], $\overline{\Delta\nu_{exp}}$: mean experimental hfs splitting [MHz], a) parameter held fixed, b) parameter constrained (planarity condition), *: dependent on $\measuredangle$ (OD, a); standard errors in units of the last digit in brackets.

Watson's a-reduction		Watson's s-reduction		Correlation matrix					
A	12 971.717(18)	A	12 971.716(19)	1.00					
B	11 308.482(15)	B	11 308.468(18)	0.83	1.00				
C	6 033.985(15)	C	6 034.003(13)	0.69	0.88	1.00			
Δ_J	13.3(20)	D_J	11.5(23)	0.89	0.93	0.90	1.00		
Δ_{JK}	– 17.8(12)	D_{JK}	– 18.6(13)	– 0.46	– 0.02	0.24	– 0.15	1.00	
Δ_K	0.0 a	D_K	8.2(14) b						
δ_J	– 0.35(19)	d_1	0.19(22)	– 0.47	0.05	0.17	– 0.16	0.92	1.00
δ_K	0.0 a	d_2	0.0 a						
N	12	N	12						
σ	21	σ	25						
χ_+	0.0296(83)	χ_{aa}	– 0.0296(83)	$\measuredangle$ (OD, a)		53.7(5)°			
χ_-	0.2893(94)	χ_{bb}	0.1595(89)	χ_{zz}*		0.382			
N	5	χ_{cc}	– 0.1299(89)	χ_{xx}*		– 0.252			
$\lvert(\chi_+, \chi_-)\rvert$	0.117	χ_{ab}*	– 0.302	χ_{yy}*		– 0.130			
$\overline{\Delta\nu_{exp}}$	0.052								

correlation coefficient $|(\chi_+, \chi_-)|$ of χ_+ and χ_-, the mean D-hfs splitting and the standard deviation of the fit.

As an r_s-structure for HNO_3 already had been determined [4], we were able to transform the coupling tensor to the O-D bond axis system. Unfortunately the r_s-structure cannot be calculated for $D^{15}NO_3$ as mother molecule from the available data, because the spectrum of $D^{18}O^{15}NO_2$ has not been analysed.

Table 3. Bond axis coupling tensor components [MHz] of OD-bonds. z: bond axis, x: in molecular plane, y: perpendicular to molecular plane.

	χ_{zz}	χ_{xx}	χ_{yy}
HOD [10]	0.3132	− 0.1477	− 0.1658
CH_3OD [11]	0.303	–	–
trans-HCOOD [5]	0.272	− 0.124	− 0.148
$O_2{}^{15}NOD$ [this work]	0.382	− 0.252	− 0.130

So we took the r_s-structure of Table V, column I of [4], substituted deuterium and ^{15}N masses and calculated the coordinates in the $D^{15}NO_3$-principal inertia axis system.

We determined the angle of the OD bond with respect to the a-inertia axis to be $\sphericalangle$ (OD, a) = 53.7° ± 0.5°. The error is estimated. From an r_0-calculation fitting the rotational constants of the eight isotopic species we get $\sphericalangle$ (OD, a) = 53.9° ± 0.5°.

The transformation to an x, y, z-bond axis system with the z-axis collinear to the OD-bond, the x-axis in the molecular plane and the y-axis collinear to the c-axis first leads to the calculation of a χ_{ab} and secondly to values for χ_{gg}, $g = x, y, z$, given in Table 2.

The sign of χ_{ab} depends on the choice that the OD-bond was arbitrarily placed in the first a,b-quadrant. The calculation of χ_{ab} and χ_{gg}, $g = x, y, z$ depends on the assumption that the coupling tensor has a principal axis collinear with the OD-bond, which may be doubted.

In Table 3 we compare our result with coupling tensors of related molecules, which were investigated with molecular beam methods.

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