Nitrogen and Deuterium Hyperfine Structure in the Rotational Spectrum of Morpholine

J.-U. Grabow, H. Ehrlichmann, and H. Dreizler

Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

Z. Naturforsch. **44a**, 833–836 (1989); received July 18, 1989

We reinvestigated the rotational spectra of morpholine and N-deutero morpholine with the higher precision of microwave Fourier transform spectroscopy. The rotational, centrifugal, and nitrogen quadrupole coupling constants were improved and the deuterium quadrupole coupling constants determined.

Introduction

The microwave spectrum of morpholine, OC_4H_8N–H and OC_4H_8N–D was first investigated by Sloan and Kewley [1]. They attributed the assigned spectrum to a chair form with the hydrogen in an equatorial position. They determined the ^{14}N quadrupole coupling constants and the dipole moment. Later Filgueira, Fantoni, and Boggia [2] performed a centrifugal distortion analysis of the normal isotopomer.

We reinvestigated the spectra to improve the accuracy of the ^{14}N quadrupole coupling constants and to determine the deuterium quadrupole constants of D bound to nitrogen by using microwave Fourier transform (MWFT) spectroscopy [3].

Experimental

We used commercial morpholine. The deuterated isotopomer was prepared by mixing 1 ml of morpholine with 4 ml of a 40% sodium deuterooxide (NaOD) solution in D_2O (99 atom% D). After shaking this mixture for a few minutes in a separatory funnel two phases could be separated. The upper phase containing the N-deuterated morpholine was good enough to be used for our measurements without further purifications.

The spectra were recorded by our MWFT spectrometers from 4 to 18 GHz [4–6]. The temperature was about 220 K, the pressure between 0.5 and 3 mTorr (0.1 to 0.4 Pa). The frequencies of the multiplet components were determined by a least squares fit of the time domain signal [7] to avoid overlapping effects. Parts of the measurements are given in Tables 1 and 2. A complete list is available under number TNA 18 at the Universitätsbibliothek, Westring 400, D-2300 Kiel.

Analysis

We used the multiplet splittings of our measurements (complete list) to determine the ^{14}N quadrupole coupling constants by diagonalizing the hamiltonian matrix neglecting elements off diagonl in the angular momentum quantum number J (programme SUZIQS [8]). For the deuterated isotopomer first order theory with the coupling scheme $F_1 = J + I_1$ and $F = F_1 + I_2$ was used [9] (programme Q2FIT/Q2SIM [10]). The results are given in Table 3. In addition a centrifugal distortion analysis with the S reduction of Watson for the III^r representation [11] was performed mainly to verify the assignment. The hypothetical center frequencies ν_0 of the transitions we measured were calculated by the programme SUZIQS [8]. We included the lines given in Table 1 of [1]. To get the hypothetical center frequencies ν_0 of these transitions, the frequencies were corrected by the splittings calculated in course of the hfs analysis. Because of the lower accuracy of the Stark measurements those transitions that do not agree with the calculated frequencies within the triplet standard deviation have not been used in the final fit. Table 4 gives typical correlation matrices for the analysis.

Reprint requests to Prof. Dr. H. Dreizler, Abteilung Chemische Physik im Institut für Physikalische Chemie, Christian-Albrechts-Universität, Olshausenstr. 40, D-2300 Kiel.

0932-0784 / 89 / 0900-0833 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1. Part of measured transitions of morpholine H equatorial. Experimental frequency of a component ν_{obs}, hfs splitting $\Delta\nu_{hfs} = \nu_{obs} - \nu_0$, deviation of the hfs analysis $\delta\Delta_{calc-obs}$, hypothetical unsplit line ν_0, deviation of the centrifugal distortion analysis $\delta\nu_{calc-obs}$.

$J, K_-, K_+ - J', K'_-, K'_+$ $F - F'$	ν_{obs}/ GHz	ν_0/ GHz	$\Delta\nu_{hfs}$/ MHz	$\delta\nu_{calc-obs}$/ kHz	$\delta\Delta\nu_{calc-obs}$/ kHz
1, 0, 1 − 0, 0, 0		7.309373		−20	
2 − 1	7.309267		−0.107		− 1
1 − 1	7.309908		0.534		3
0 − 1	7.308301		−1.073		− 2
1, 1, 0 − 0, 0, 0		9.550117		−14	
2 − 1	9.550365		0.248		− 1
1 − 1	9.548878		−1.239		3
0 − 1	9.552597		2.480		− 7
2, 1, 1 − 2, 1, 2		5.822614		10	
3 − 3	5.823167		0.553		0
2 − 2	5.820680		−1.934		− 1
1 − 1	5.824547		1.933		3
2 − 3	5.822265		−0.349		3
1 − 2	5.822078		−0.536		− 1
3 − 2	5.821576		−1.038		1
2, 2, 1 − 2, 0, 2		6.754359		12	
3 − 3	6.754860		0.501		0
2 − 2	6.752604		−1.755		2
1 − 1	6.756113		1.754		− 1
2 − 3	6.754172		−0.187		− 3
1 − 2	6.753681		−0.678		0
3 − 2	6.753299		−1.060		− 2
2 − 1	6.755050		0.691		−13
2, 0, 2 − 1, 0, 1		12.945598		−24	
3 − 2	12.945358		−0.240		0
2 − 1	12.946274		0.676		2
1 − 0	12.945459		−0.139		− 2
2 − 2	12.946922		1.324		− 2
1 − 1	12.943845		−1.753		0
2, 1, 1 − 1, 1, 0		16.559602		−19	
3 − 2	16.559554		−0.048		0
2 − 1	16.560139		0.537		0
1 − 0	16.557826		−1.776		2
2 − 2	16.558657		−0.945		− 2
1 − 1	16.561536		1.934		1
2, 1, 2 − 1, 1, 1		12.677862		−25	
3 − 2	12.677649		−0.213		0
2 − 1	12.678399		0.537		0
1 − 0	12.678020		0.158		4
2 − 2	12.679236		1.374		2
1 − 1	12.675927		−1.935		0
4, 3, 2 − 4, 1, 3		10.571470		24	
5 − 5	10.571799		0.329		0
4 − 4	10.570567		−0.903		0
3 − 3	10.572115		0.645		0
4, 1, 3 − 4, 1, 4		14.568198		45	
5 − 5	14.568676		0.478		0
4 − 4	14.566886		−1.312		0
3 − 3	14.569135		0.937		1
5, 3, 3 − 5, 1, 4		14.566050		42	
6 − 6	14.566385		0.335		0
5 − 5	14.565178		−0.872		0
4 − 4	14.566630		0.580		1
7, 5, 3 − 7, 3, 4		14.573293		36	
8 − 8	14.573481		0.188		1
7 − 7	14.572836		−0.457		− 1
6 − 6	14.573575		0.282		0
11, 10, 2 − 11, 9, 2		10.381007		−12	
12 − 12	10.380942		−0.065		9
11 − 11	10.381139		0.132		− 4
10 − 10	10.380942		−0.065		− 8
15, 12, 3 − 15, 12, 4		5.657218		−14	
16 − 16	5.657304		0.086		−10
15 − 15	5.657044		−0.174		6
14 − 14	5.657304		0.086		6

Table 2. Part of measured transitions of morpholine D equatorial. Experimental frequency of a component ν_{obs}, hfs splitting with respect to the strongest hfs component $\Delta\nu_{hfs}=\nu_{obs}-\nu'_{obs}$, deviation of the hfs analysis $\delta\Delta\nu_{calc-obs}$, hypothetical unsplit line ν_0, deviation of the centrifugal distortion analysis $\delta\nu_{calc-obs}$.

$J, K_-, K_+ - J', K'_-, K'_+$ $2F_1, 2F - 2F'_1, 2F'$	ν_{obs}/ GHz	ν_0/ GHz	$\Delta\nu_{hfs}$/ MHz	$\delta\nu_{calc-obs}$/ kHz	$\delta\Delta\nu_{calc-obs}$/ kHz
2, 1, 1 − 1, 1, 0		15.806103		65	
2, 4 − 0, 2	15.804321		−1.719		12
2, 2 − 0, 2					
4, 6 − 4, 6	15.805160		−0.880		− 4
6, 4 − 4, 2	15.806040				
6, 8 − 4, 6					
6, 6 − 4, 4	15.806097		0.057		7
4, 4 − 2, 2	15.806644		0.604		7
4, 6 − 2, 4					
2, 4 − 2, 4	15.808039		1.999		7
2, 1, 2 − 1, 1, 1		12.220943		55	
2, 4 − 2, 4	12.219003		−1.713		5
6, 4 − 4, 2	12.220682		−0.035		11
6, 8 − 4, 6	12.220716				
6, 6 − 4, 4	12.220775		0.058		− 1
2, 4 − 0, 2	12.221100		0.384		3
2, 2 − 0, 2					
4, 6 − 2, 4	12.221484		0.768		1
4, 4 − 2, 2					
2, 0, 2 − 1, 0, 1		12.647110		63	
2, 4 − 2, 4	12.645386		−1.500		−12
6, 6 − 4, 4	12.646886				
6, 8 − 4, 6					
6, 4 − 4, 2					
2, 4 − 0, 2	12.647018		0.132		− 2
2, 2 − 0, 2					
4, 6 − 2, 4	12.647729		0.842		23
3, 2, 1 − 3, 2, 2		4.658342		13	
6, 4 − 6, 4	4.657352		−1.308		− 2
6, 8 − 6, 8					
6, 6 − 6, 6					
8, 6 − 8, 6	4.658660				
8, 10 − 8, 10					
8, 8 − 8, 8	4.658691		0.031		− 7
4, 2 − 4, 2	4.659130		0.470		− 8
4, 6 − 4, 6					
4, 4 − 4, 4	4.659149		0.489		− 7
4, 3, 2 − 4, 1, 3		10.664140		23	
8, 8 − 8, 8	10.663245		−1.223		− 1
8, 10 − 8, 10	10.663288		−1.181		− 2
8, 6 − 8, 6					
10, 10 − 10, 10	10.664424		−0.045		− 2
10, 12 − 10, 12	10.664468				
10, 8 − 10, 8					
6, 6 − 6, 6	10.664726		0.257		1
6, 8 − 6, 8	10.664771		0.303		− 1
6, 4 − 6, 4					
8, 5, 3 − 8, 5, 4		11.206394		6	
16, 14 − 16, 14	11.205895		−0.697		3
16, 18 − 16, 18					
16, 16 − 16, 16	11.205919		−0.673		4
18, 16 − 18, 16	11.206591				
18, 20 − 18, 20					
18, 18 − 18, 18	11.206619		0.027		− 1
14, 12 − 14, 12	11.206677		0.086		2
14, 16 − 14, 16					
14, 14 − 14, 14	11.206709		0.118		− 4
9, 7, 3 − 9, 6, 3		5.847546		−16	
20, 20 − 20, 20	5.847432		−0.052		13
16, 18 − 16, 18					
16, 14 − 16, 14					
20, 22 − 20, 22	5.847484				
20, 18 − 20, 18					
18, 18 − 18, 18	5.847705		0.221		− 7
18, 20 − 18, 20	5.847749		0.265		4
18, 16 − 18, 16					
15, 11, 4 − 15, 11, 5		5.372012		−19	
30, 28 − 30, 28	5.371812		−0.280		0
30, 32 − 30, 32					
30, 30 − 30, 30	5.371836		−0.256		0
32, 30 − 32, 30	5.372092				
32, 34 − 32, 34					
28, 26 − 28, 26	5.372115		0.024		− 3
28, 30 − 28, 30					
32, 32 − 32, 32					
28, 28 − 28, 28	5.372132		0.041		2

It should be pointed out that the χ_{bb} values of both isotopomers agree reasonably. An estimate of the principal coupling tensor elements using the different position of the isotopomers in their principal inertia axes system was not possible as the rotation by deuteration is too small.

Table 3. Rotational constants A, B, C, quartic centrifugal distortion constants of Watson's S reduction D_J, D_{JK}, D_K, d_1, d_2, Ray's asymmetry parameter $\varkappa$, number of fitted lines N_L, standard deviation of the fit of the centrifugal distortion analysis σ_{cd}, quadrupole coupling constants χ, number of fitted hfs components N_c, mean splitting $\overline{\Delta\nu_{hfs}}$, standard deviation of the fit of the quadrupole coupling analysis σ_{hfs}, correlation of the quadrupole coupling constants $|(\chi^+, \chi^-)|$. Standard errors in parenthesis (in units of the least significant digit).

OC_4H_8N-H		OC_4H_8N-D	
A/GHz	4.9249875(53)	A/GHz	4.925567(14)
B/GHz	4.6251166(53)	B/GHz	4.399697(13)
C/GHz	2.6842359(54)	C/GHz	2.607105(14)
D_J/kHz	0.38(25)	D_J/kHz	1.26(43)
D_{JK}/kHz	−1.746(17)	D_{JK}/kHz	−1.670(96)
D_K/kHz	0.930(41)	D_K/kHz	0.82(11)
d_1/Hz	3.3(36)	d_1/Hz	−39.(25)
d_2/Hz	−32.8(26)	d_2/Hz	−41.(14)
$\varkappa$	0.732348	$\varkappa$	0.546363
N_L	33	N_L	26
N_L [1]	30	N_L [1]	43
σ_{cd}/kHz	36	σ_{cd}/kHz	132
χ^+(N)/MHz	−2.1491(24)	χ^+(N)/MHz	−2.166(6)
χ^-(N)/MHz	7.7422(42)	χ^-(N)/MHz	7.740(8)
χ_{aa}(N)/MHz	2.1491(24)	χ_{aa}(N)/MHz	2.166(6)
χ_{bb}(N)/MHz	2.7966(25)	χ_{bb}(N)/MHz	2.787(4)
χ_{cc}(N)/MHz	−4.9457(24)	χ_{cc}(N)/MHz	−4.953(6)
N_c	109	χ^+(D)/MHz	−0.220(10)
$\overline{\Delta\nu_{hfs}}$/kHz	539	χ^-(D)/MHz	0.004(15)
σ_{hfs}/kHz	3.72	χ_{aa}(D)/MHz	0.220(10)
$\|(\chi^+, \chi^-)\|$	0.057	χ_{bb}(D)/MHz	−0.108(6)
		χ_{cc}(D)/MHz	−0.112(11)
		N_c	113
		σ_{hfs}/kHz	6.49

Acknowledgements

We thank the members of our group for help and discussion, especially M. Andolfatto for preparing the deuterated substance, the Deutsche Forschungsgemeinschaft, the Land Schleswig-Holstein, and the Fonds der Chemie for funds. The calculations were made at the Rechenzentrum of the University of Kiel.

[1] J. J. Sloan and R. Kewley, Can. J. Chem. **47,** 3453 (1969); Can. J. Chem. **50,** 955 (1972), erratum.
[2] R. R. Filgueira, A. C. Fantoni, and L. M. Boggia, J. Mol. Spectrosc. **78,** 175 (1979).
[3] H. Dreizler, Mol. Phys. **59,** 1 (1986).
[4] H. Ehrlichmann, J.-U. Grabow, H. Dreizler, N. Heineking, R. Schwarz, and U. Andresen, Z. Naturforsch. **44a,** 751 (1989).
[5] G. Bestmann, H. Dreizler, E. Fliege, and W. Stahl, J. Mol. Struct. **97,** 215 (1983).
[6] G. Bestmann and H. Dreizler, Z. Naturforsch. **37a,** 58 (1982).
[7] J. Haekel and H. Mäder, Z. Naturforsch. **43a,** 203 (1988).
[8] Author: O. Böttcher, Kiel.
[9] W. Gordy and R. L. Cook, Mikrowave Molecular Spectra, John Wiley, New York 1984, Chapt. IX and XV.
[10] Authors: D. Hübner and W. Stolze, Kiel; K. F. Gebhardt, Gießen; J. Mulford, Tübingen.
[11] J. K. Watson, Aspects of Quartic and Sextic Centrifugal Effects on Rotational Energy Levels, in: Vibrational Spectra and Structure (J. R. Durig, ed.), Elsevier, New York 1977, p. 36.

Table 4. Correlation matrices for values of Table 3. a) For the rotational and centrifugal distortion constants of OC_4H_8N-H. b) For the nuclear quadrupole coupling constants of OC_4H_8N-D.

A	1.000							
B	0.972	1.000						
C	0.921	0.941	1.000					
D_J	0.859	0.870	0.861	1.000				
D_{JK}	−0.033	−0.009	0.113	0.043	1.000			
D_K	−0.098	−0.066	−0.152	−0.007	−0.356	1.000		
d_1	−0.115	0.046	0.014	−0.006	0.149	0.058	1.000	
d_2	−0.051	0.018	−0.001	−0.011	−0.021	0.106	0.872	1.000
χ_{aa}(N)	1.000							
χ_{bb}(N)	−0.483	1.000						
χ_{aa}(D)	−0.221	0.211	1.000					
χ_{bb}(D)	0.076	−0.027	−0.191	1.000				