Centrifugal Distortion and Ground State Internal Rotation Analysis of the Microwave Spectrum of Dimethylsulfoxide

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The torsional fine structure of dimethylsulfoxide has been reinvestigated with MWFT-spectroscopy. The higher resolution results in a more accurate determination of the internal rotation barrier V_3. The centrifugal distortion analysis is extended to sixth order. The prediction of lines is excellent, but some centrifugal distortion constants are poorly determined.

Several years ago the microwave spectra of dimethylsulfoxide (DMSO), $(CH_3)_2SO$, and six isotopic forms were investigated [1–4]. The molecule was used to test the centrifugal distortion theory [2, 5–8]. The dipole moment [1], a complete r_s-structure [4], an r_z-structure [9] and the potential V_3 hindering the methyl internal rotation (torsion) [3, 4] were determined. The potential parameters calculated with different structural parameters of the methyl group were given in Table 6 b of [4].

With the recently developed microwave Fourier transform (MWFT) spectrometer from 8 to 18 GHz [10, 11] it was possible to resolve the fine structure of 30 lines much better than with Stark spectroscopy (see Table 1 of [3]). A comparison is given in Figure 1.

To check the assignment of the high J-lines we performed a centrifugal distortion analysis up to sixth order using the Hamiltonian proposed by Van Eijck and Typke [12, 13]:

$$\begin{aligned} H = {} & X' P_x^2 + Y' P_y^2 + Z' P_z^2 - D'_J P^4 - D'_{JK} P^2 P_z^2 \\ & - D'_K P_z^4 - 2\delta'_J P^2 (P_x^2 - P_y^2) + 2R'_6 O + H'_J P^6 \\ & + H'_{JK} P^4 P_z^2 + H'_{KJ} P^2 P_z^4 + H'_K P_z^6 \\ & + H'_5 P^4 (P_x^2 - P_y^2) + \tfrac{1}{2} H'_6 P^2 O + H'_{10} (P_x^2 - P_y^2)^3 \end{aligned} \quad (1)$$

with

$$O = P_x^4 + P_y^4 - 3(P_x^2 P_y^2 + P_y^2 P_x^2)$$

and using the Hamiltonian from Watson's S-reduction [14]:

$$\begin{aligned} H = {} & ((X' + Y')/2) P^2 + (Z' - (X' + Y')/2) P_z^2 \\ & + ((X' - Y')/4)(P_+^2 + P_-^2) - D_J P^4 - D_{JK} P^2 P_z^2 \\ & - D_K P_z^4 + d_1 P^2 (P_+^2 + P_-^2) + d_2 (P_+^4 + P_-^4) \\ & + H_J P^6 + H_{JK} P^4 P_z^2 + H_{KJ} P^2 P_z^4 + H_K P_z^6 \\ & + h_1 P^4 (P_+^2 + P_-^2) + h_2 P^2 (P_+^4 + P_-^4) \\ & + h_3 (P_+^6 + P_-^6) \end{aligned} \quad (2)$$

with

$$P_\pm = P_x \pm i P_y .$$

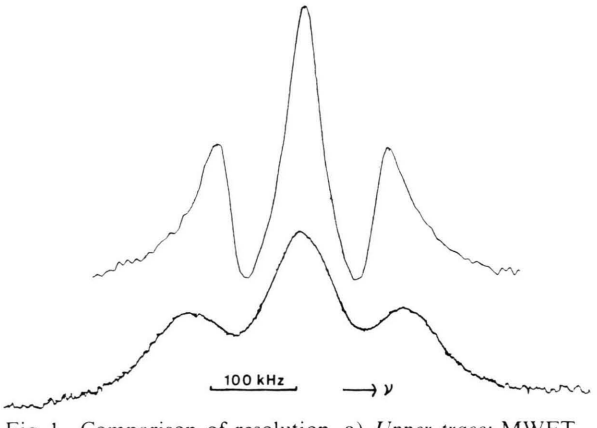

Fig. 1. Comparison of resolution. a) *Upper trace:* MWFT measurement (Kiel, 1981): DMSO: transition $18_{17,1} - 18_{16,2}$; ν_{EA}, ν_{AE}: 12.141 941 GHz, ν_{EE}: 12.141 043 GHz, ν_{AA}: 12.142 142 GHz; pressure in the sample cell; 0.2 mT; temperature: −40 °C. b) *Lower trace:* Stark measurement recorded in one direction (Freiburg, 1963): DMSO: transition $19_{19,0} - 19_{18,1}$; ν_{EA}, ν_{AE}: 19.269 396 GHz, ν_{EE}: 19.269 522 GHz, ν_{AA}: 19.269 650 GHz; pressure: 4 mT; temperature: −44 °C.

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Table 1. Measured lines ν_{exp} of DMSO ordered in series in part from [2]. *: Corrected measurements [7], FT: Measured by MWFT spectroscopy, ν_r: Calculated with rigid rotor model, ν_{calc}: Calculated with Hamiltonian (1) and constants of Table 3, $\Delta\nu$[4] and $\Delta\nu$[6]: fourth and sixth order contributions. For the centrifugal distortion analysis the weighted means of the internal rotation fine structure components were used.

J	K_-	K_+	J'	K'_-	K'_+	ν_r [GHz]	$\Delta\nu$[4] [MHz]	$\Delta\nu$[6] [MHz]	ν_{calc} [GHz]	ν_{exp} [GHz]	$\nu_{calc}-\nu_{exp}$ [MHz]
1	1	1	0	0	0	11.255357	− 0.010	0.000	11.255347	11.255350	−0.003
2	0	2	1	1	1	19.562855	− 0.063	−0.002	19.562790	19.562768	0.022
2	1	2	1	0	1	19.692911	− 0.048	−0.002	19.692861	19.692873	−0.012
2	2	0	1	1	1	30.591168	− 0.197	−0.002	30.590969	30.590986	−0.017
2	2	1	1	1	0	25.328517	− 0.133	−0.002	25.328382	25.328372	0.010
3	0	3	2	1	2	28.064851	− 0.157	−0.016	28.064678	28.064628	0.050
3	1	2	2	2	1	33.367329	− 0.367	−0.012	33.366949	33.366944	0.005
3	1	3	2	0	2	28.069247	− 0.143	−0.016	28.069088	28.069145	−0.057
3	2	2	2	1	1	33.766071	− 0.287	−0.012	33.765771	33.765770	0.001
4	1	4	3	0	3	36.504532	− 0.314	−0.073	36.504145	36.504145	0.000
9	9	0	9	8	1	6.496751	0.593	0.003	6.497347	6.497341	0.006
10	10	0	10	9	1	7.485239	0.803	0.006	7.486048	7.486040	0.008
11	11	0	11	10	1	8.590711	0.811	0.011	8.591533	8.591558	−0.025
12	12	0	12	11	1	9.796751	0.396	0.019	9.797166	9.797151 FT	0.015
13	13	0	13	12	1	11.082532	− 0.718	0.031	11.081845	11.081813	0.032
14	14	0	14	13	1	12.425051	− 2.837	0.049	12.422263	12.422247	0.016
15	15	0	15	14	1	13.801532	− 6.257	0.075	13.795349	13.795329	0.020
16	16	0	16	15	1	15.191648	−11.231	0.111	15.180528	15.180529 FT	−0.001
17	17	0	17	16	1	16.579186	−17.936	0.160	16.561410	16.561410	0.000
18	18	0	18	17	1	17.952842	−26.478	0.225	17.926589	17.926598	−0.009
19	19	0	19	18	1	19.306094	−36.903	0.311	19.269501	19.269507 *	−0.006
20	20	0	20	19	1	20.636379	−49.233	0.421	20.587566	20.587575	−0.009
21	21	0	21	20	1	21.943948	−63.487	0.562	21.881023	21.881036	−0.013
22	22	0	22	21	1	23.230750	−79.698	0.739	23.151792	23.151798	−0.006
23	23	0	23	22	1	24.499536	−97.922	0.960	24.402573	24.402572	0.001
25	25	0	25	24	1	26.994690	−140.739	1.563	26.855514	26.855504	0.010
2	2	1	2	1	2	8.453408	− 0.095	0.000	8.453314	8.453292	0.022
3	3	1	3	2	2	8.644683	− 0.264	0.000	8.644419	8.644356	0.063
4	4	1	4	3	2	8.901177	− 0.503	0.000	8.900674	8.900682	−0.008
5	5	1	5	4	2	9.223880	− 0.826	0.000	9.223054	9.223090	−0.036
6	6	1	6	5	2	9.613716	− 1.254	0.000	9.612462	9.612492	−0.030
7	7	1	7	6	2	10.071362	− 1.817	0.001	10.069546	10.069578	−0.032
8	8	1	8	7	2	10.597068	− 2.555	0.002	10.594515	10.594531	−0.016
9	9	1	9	8	2	11.190485	− 3.521	0.003	11.186967	11.186985 *	−0.018
10	10	1	10	9	2	11.850532	− 4.785	0.006	11.845753	11.845755	−0.002
11	11	1	11	10	2	12.575307	− 6.432	0.011	12.568886	12.568902	−0.016
12	12	1	12	11	2	13.362064	− 8.563	0.019	13.353520	13.353532	−0.012
13	13	1	13	12	2	14.207251	−11.298	0.031	14.195985	14.195998	−0.013
14	14	1	14	13	2	15.106612	−14.769	0.048	15.091891	15.091885	0.006
15	15	1	15	14	2	16.055335	−19.124	0.074	16.036285	16.036273 FT	0.012
16	16	1	16	15	2	17.048243	−24.516	0.109	17.023837	17.023827 FT	0.010
2	1	1	2	0	2	8.080454	− 0.093	0.000	8.080361	8.080377	−0.016
3	2	1	3	1	2	7.911742	− 0.241	0.000	7.911501	7.911510	−0.009
4	3	1	4	2	2	7.708510	− 0.414	0.000	7.708097	7.708091	0.006
5	4	1	5	3	2	7.488950	− 0.576	0.000	7.488374	7.488320 *	0.054
6	5	1	6	4	2	7.274691	− 0.672	0.000	7.274019	7.274020	−0.001
7	6	1	7	5	2	7.089406	− 0.623	0.000	7.088783	7.088791	−0.008
8	7	1	8	6	2	6.957018	− 0.323	−0.001	6.956694	6.956698	−0.004
9	8	1	9	7	2	6.899965	0.356	−0.001	6.900320	6.900321	−0.001
10	9	1	10	8	2	6.938067	1.562	−0.002	6.939628	6.939623	0.005
12	11	1	12	10	2	7.364688	6.232	−0.003	7.370917	7.370970	−0.053
13	12	1	13	11	2	7.779313	10.042	−0.004	7.789351	7.789385	−0.034
14	13	1	14	12	2	8.341330	15.017	−0.004	8.356343	8.356329	0.014
15	14	1	15	13	2	9.056421	21.190	−0.004	9.077606	9.077625	−0.019
16	15	1	16	14	2	9.925396	28.443	−0.003	9.953836	9.953817 FT	0.019
17	16	1	17	15	2	10.942985	36.472	−0.001	10.979455	10.979460	−0.005
18	17	1	18	16	2	12.097285	44.768	0.002	12.142056	12.142044	0.012
19	18	1	19	17	2	13.370172	52.659	0.008	13.422839	13.422824	0.015
20	19	1	20	18	2	14.738656	59.365	0.017	14.798038	14.798038 FT	0.000

Table 1 (continued).

J	K_-	K_+	J'	K'_-	K'_+	ν_r [GHz]	$\Delta\nu$[4] [MHz]	$\Delta\nu$[6] [MHz]	ν_{calc} [GHz]	ν_{exp} [GHz]	$\nu_{calc}-\nu_{exp}$ [MHz]
21	20	1	21	19	2	16.176930	64.107	0.030	16.241067	16.241072 FT	−0.005
22	21	1	22	20	2	17.658775	66.206	0.048	17.725028	17.725040 FT	−0.012
3	2	2	3	1	3	13.777277	− 0.238	0.004	13.777044	13.776961	0.083
4	3	2	4	2	3	13.788963	− 0.529	0.004	13.788437	13.788393	0.044
5	4	2	5	3	3	13.812372	− 0.845	0.003	13.811531	13.811486	0.045
7	6	2	7	5	3	13.916481	− 1.418	0.002	13.915065	13.915032	0.033
17	16	2	17	15	3	17.110196	4.901	−0.022	17.115076	17.115057 FT	0.019
18	17	2	18	16	3	17.772167	6.253	−0.024	17.778397	17.778380 FT	0.017
24	22	2	24	21	3	14.111156	133.963	0.149	14.245267	14.245254 FT	0.013
25	23	2	25	22	3	15.299876	162.521	0.179	15.462577	15.462575 FT	0.002
26	24	2	26	23	3	16.626899	190.161	0.209	16.817269	16.817277 FT	−0.008
3	1	2	3	0	3	13.755886	− 0.305	0.004	13.755585	13.755598	−0.013
4	2	2	4	1	3	13.725391	− 0.733	0.004	13.724662	13.724686	−0.024
5	3	2	5	2	3	13.666161	− 1.323	0.003	13.664841	13.664857	−0.016
6	4	2	6	3	3	13.566514	− 2.110	0.003	13.564407	13.564458	−0.051
8	6	2	8	5	3	13.206482	− 4.374	0.002	13.202110	13.202112	−0.002
9	7	2	9	6	3	12.936865	− 5.832	0.002	12.931035	12.931025	0.010
10	8	2	10	7	3	12.612161	− 7.407	0.002	12.604756	12.604742	0.014
11	9	2	11	8	3	12.245115	− 8.931	0.002	12.236186	12.236177	0.009
13	11	2	13	10	3	11.467098	−10.735	0.004	11.456367	11.456357	0.010
14	12	2	14	11	3	11.108507	−10.278	0.006	11.098235	11.098264	−0.029
15	13	2	15	12	3	10.808060	− 8.340	0.009	10.799729	10.799724	0.005
16	14	2	16	13	3	10.593191	− 4.472	0.013	10.588732	10.588731	0.001
18	16	2	18	15	3	10.515195	10.776	0.027	10.525998	10.525991	0.007
19	17	2	19	16	3	10.690207	22.940	0.038	10.713184	10.713178	0.006
20	18	2	20	17	3	11.026933	38.551	0.052	11.065536	11.065592	−0.056
21	19	2	21	18	3	11.534871	57.757	0.071	11.592698	11.592701	−0.003
22	20	2	22	19	3	12.219219	80.451	0.093	12.299763	12.299760	0.003
23	21	2	23	20	3	13.080011	106.157	0.120	13.186288	13.186274	0.014
27	25	2	27	24	3	18.067552	215.066	0.235	18.282853	18.282859	−0.006
4	2	3	4	1	4	19.276851	− 0.552	0.023	19.276323	19.276240	0.083
5	3	3	5	2	4	19.272566	− 1.167	0.021	19.271420	19.271395	0.025
6	4	3	6	3	4	19.266016	− 1.892	0.019	19.264144	19.264216 *	−0.072
7	5	3	7	4	4	19.257170	− 2.709	0.017	19.254478	19.254445	0.033
8	6	3	8	5	4	19.246533	− 3.595	0.015	19.242953	19.242940	0.013
9	7	3	9	6	4	19.235314	− 4.510	0.013	19.230816	19.230805	0.011
10	8	3	10	7	4	19.225561	− 5.405	0.011	19.220167	19.220158	0.009
11	9	3	11	8	4	19.220246	− 6.211	0.009	19.214044	19.214034	0.010
12	10	3	12	9	4	19.223281	− 6.845	0.007	19.216444	19.216436	0.008
13	11	3	13	10	4	19.239471	− 7.208	0.005	19.232269	19.232261	0.008
15	13	3	15	12	4	19.334220	− 6.661	0.003	19.327562	19.327578	−0.016
4	1	3	4	0	4	19.276209	− 0.560	0.023	19.275672	19.275737	−0.065
5	2	3	5	1	4	19.270007	− 1.200	0.021	19.268828	19.268850	−0.022
6	3	3	6	2	4	19.258385	− 1.990	0.019	19.256414	19.256450	−0.036
7	4	3	7	3	4	19.238245	− 2.957	0.017	19.235304	19.235329	−0.025
8	5	3	8	4	4	19.205336	− 4.145	0.014	19.201206	19.201221	−0.015
9	6	3	9	5	4	19.154045	− 5.617	0.011	19.148439	19.148449	−0.010
10	7	3	10	6	4	19.077274	− 7.465	0.009	19.069817	19.069831	−0.014
11	8	3	11	7	4	18.966508	− 9.806	0.005	18.956708	18.956717	−0.009
12	9	3	12	8	4	18.812203	−12.770	0.002	18.799435	18.799446	−0.011
13	10	3	13	9	4	18.604634	−16.484	−0.001	18.588149	18.588155	−0.006
14	11	3	14	10	4	18.335268	−21.023	−0.004	18.314241	18.314244	−0.003
15	12	3	15	11	4	17.998583	−26.356	−0.007	17.972221	17.972226	−0.005
16	13	3	16	12	4	17.594017	−32.283	−0.009	17.561725	17.561703	0.022
20	17	3	20	16	4	15.524355	−50.194	0.004	15.474165	15.474148 FT	0.017
30	27	3	30	26	4	16.065775	256.633	0.784	16.323192	16.323184 FT	0.008
31	28	3	31	27	4	17.093025	322.794	0.953	17.416773	17.416772 FT	0.001
5	1	4	5	0	5	24.785450	− 0.962	0.079	24.784567	24.784552	0.015
30	26	4	30	25	5	17.734957	−100.657	0.172	17.634472	17.634471 FT	0.001
31	27	4	31	26	5	17.349261	−58.394	0.357	17.291223	17.291224 FT	−0.001
34	30	4	34	29	5	17.210608	160.698	1.286	17.372592	17.372598 FT	−0.006
35	31	4	35	30	5	17.565669	263.804	1.732	17.831205	17.831204 FT	0.001

Table 2. μ_c-transitions of DMSO. ν_{exp}: measured by RF-double resonance with pump frequency adjustment. ν_{calc}: see Table 1. In brackets signal transitions.

J	K_-	K_+	J'	K'_-	K'_+	ν_{exp} [GHz]	ν_{calc} [GHz]
13	13	1	13	12	1	10.769325	10.769037
(13	13	1	13	12	2)		
9	8	2	9	7	2	1.290650	1.290304
(9	7	2	9	6	3)		
(9	8	2	9	7	3)		
10	9	2	10	8	2	1.858860	1.858765
(10	8	2	10	7	3)		
(10	9	2	10	8	3)		
14	12	3	14	11	3	1.024292	1.024292
(14	13	2	14	12	3)		
15	13	3	15	12	3	1.477105	1.477104
(15	14	2	15	13	3)		
20	17	4	20	16	4	1.054571	1.054571
(20	17	3	20	16	4)		
21	18	4	21	17	4	1.489850	1.489386
(21	18	3	21	17	4)		

The fourth order part is treated by diagonalisation, the sixth order is introduced by first order perturbation. With the representation III^r the rotational constants are: $X' = A$, $Y' = B$, $Z' = C$.

In fitting the rotation and centrifugal distortion constants to the lines of Table 1, we noticed a high correlation $|(A, B)| = 0.999$ of A and B. The use of $(A + B)/2$, $C - (A + B)/2$ and b_0 instead of the rotational constants A, B and C reduced the highest correlation to 0.94. We tried further to reduce the A, B-correlation by including the μ_c-transitions of Table 2. They were measured with double resonance [15] using a pump frequency adjustment and a μ_b-transition as the signal. The μ_c-lines are very weak and with one exception not in the range of our FT and Stark spectrometers. The accuracy of the measurements is estimated to be 100 kHz. The

Table 3. Rotational [GHz] and centrifugal distortion constants [kHz, Hz] with standard errors due to van Eijck-Typke and Watson's S-reduction. b_0: Wang's oblate asymmetry parameter, σ: standard error of the fit, $|(x, y)|$: correlation coefficient of parameters x and y. Derived parameters below the line. For the determinable constants see [14], p. 38–41.

van Eijck-Typke			Watson's S-reduction		
$(A + B)/2$	6.9737035	(78) GHz	$(A + B)/2$	6.9737046	(78) GHz
$C - (A + B)/2$	− 2.7549265	(29) GHz	$C - (A + B)/2$	− 2.7549292	(29) GHz
b_0	− 0.022823234	(63)	b_0	− 0.022823211	(63)
D'_J	5.93	(87) kHz	D_J	5.93	(87) kHz
D'_{JK}	− 8.912	(12) kHz	D_{JK}	− 8.912	(12) kHz
D'_K	3.86	(29) kHz	D_K	3.86	(29) kHz
δ'_J	− 0.16339	(34) kHz	d_1	0.16336	(34) kHz
R'_6	− 0.271965	(90) kHz	d_2	− 0.271966	(90) kHz
H'_J	− 8.	(28) Hz	H_J	− 8.	(28) Hz
H'_{JK}	− 0.046	(34) Hz	H_{JK}	− 0.045	(34) Hz
H'_{KJ}	1.08	(91) Hz	H_{KJ}	1.08	(91) Hz
H'_K	− 7.9	(85) Hz	H_K	− 7.9	(85) Hz
H'_S	− 0.00192	(61) Hz	h_1	0.00237	(39) Hz
H'_6	0.00563	(64) Hz	h_2	0.00146	(16) Hz
H'_{10}	0.01145	(83) Hz	h_3	0.00143	(10) Hz
σ	26	kHz	σ	26	kHz
$\|(D'_J, H'_J)\|$	0.975	kHz	$\|(D_J, H_J)\|$	0.975	kHz
$\|(R'_6, H'_6)\|$	0.950	kHz	$\|(d_1, h_1)\|$	0.976	kHz
A	7.0365798	(78) GHz		7.0365809	(78) GHz
B	6.9108272	(78) GHz		6.9108283	(78) GHz
C	4.2187770	(83) GHz		4.2187754	(83) GHz
$\mathfrak{A}$	7.0365831	(95) GHz		7.0365831	(95) GHz
$\mathfrak{B}$	6.9108298	(95) GHz		6.9108298	(95) GHz
$\mathfrak{C}$	4.2187856	(98) GHz		4.2187856	(98) GHz
τ_{aaaa}	− 24.6	(35) kHz		− 24.6	(35) kHz
τ_{bbbb}	− 27.2	(35) kHz		− 27.2	(35) kHz
τ_{cccc}	− 3.5	(37) kHz		− 3.5	(37) kHz
τ_1	− 29	(10) kHz		− 29	(10) kHz
$\tau_2/(A + B + C)$	− 8.5	(35) kHz		− 8.5	(35) kHz

Table 4. Resolved internal rotation components of DMSO. ν_{AA}: AA species components, $\nu_{AA} - \nu_{\Gamma\Gamma'}$, $\Gamma\Gamma' = EE, EA, AE$: internal rotation splittings.

J	K_-	K_+	J'	K'_-	K'_+	ν_{AA}	$\nu_{AA} - \nu_{EE}$ $\nu_{AA} - \nu_{EA}$ $\nu_{AA} - \nu_{AE}$		$\Delta\nu_{exp} - \Delta\nu_{calc}$
						[GHz]	exp. [MHz]	calc. [MHz]	
11	11	0	11	10	1	8.591594	0.079	0.080	−0.001
							0.153	0.160	−0.007
							0.153	0.160	−0.007
12	12	0	12	11	1	9.797242	0.091	0.093	−0.002
							0.181	0.185	−0.004
							0.181	0.185	−0.004
13	13	0	13	12	1	11.081929	0.099	0.105	−0.006
							0.200	0.210	−0.010
							0.200	0.210	−0.010
14	14	0	14	13	1	12.422368	0.117	0.116	0.001
							0.234	0.227	0.007
							0.234	0.232	0.002
15	15	0	15	14	1	13.795465	0.120	0.125	−0.005
							0.240	0.244	−0.004
							0.240	0.251	−0.011
16	16	0	16	15	1	15.180655	0.126	0.134	−0.008
							0.252	0.257	−0.005
							0.252	0.268	−0.016
17	17	0	17	16	1	16.561549	0.138	0.141	−0.003
							0.277	0.267	0.010
							0.277	0.283	−0.006
18	18	0	18	17	1	17.926735	0.141	0.142	−0.001
							0.289	0.273	0.016
							0.289	0.296	−0.007
9	9	1	9	8	2	11.187003	0.044	0.042	0.002
							0.087	0.084	0.003
							0.087	0.084	0.003
14	14	1	14	13	2	15.091974	0.096	0.086	0.010
							0.188	0.177	0.011
							0.188	0.172	0.016
15	15	1	15	14	2	16.036379	0.106	0.096	0.010
							0.205	0.198	0.007
							0.205	0.191	0.014
16	16	1	16	15	2	17.023943	0.116	0.105	0.011
							0.233	0.221	0.012
							0.233	0.211	0.022
14	13	1	14	12	2	8.356373	0.050	0.048	0.002
							0.101	0.096	0.005
							0.101	0.096	0.005
15	14	1	15	13	2	9.077647	0.061	0.062	−0.001
							0.124	0.123	0.001
							0.124	0.123	0.001
16	15	1	16	14	2	9.953893	0.076	0.076	0.000
							0.152	0.152	0.000
							0.152	0.152	0.000
17	16	1	17	15	2	10.979524	0.087	0.091	−0.004
							0.174	0.182	−0.008
							0.174	0.182	−0.008
18	17	1	18	16	2	12.142142	0.099	0.105	−0.006
							0.201	0.210	−0.009
							0.201	0.210	−0.009
19	18	1	19	17	2	13.422951	0.121	0.118	0.003
							0.234	0.236	−0.002
							0.234	0.236	−0.002
20	19	1	20	18	2	14.798162	0.124	0.129	−0.005
							0.247	0.259	−0.012
							0.247	0.259	−0.012

Table 4 (continued).

J	K_-	K_+	J'	K'_-	K'_+	ν_{AA}	$\nu_{AA}-\nu_{EE}$ $\nu_{AA}-\nu_{EA}$ $\nu_{AA}-\nu_{AE}$		$\Delta\nu_{exp}-\Delta\nu_{calc}$
						[GHz]	exp. [MHz]	calc. [MHz]	
21	20	1	21	19	2	16.241210	0.138	0.139	−0.001
							0.273	0.278	−0.005
							0.273	0.278	−0.005
22	21	1	22	20	2	17.725185	0.145	0.146	−0.001
							0.289	0.293	−0.004
							0.289	0.293	−0.004
17	16	2	17	15	3	17.115125	0.068	0.061	0.007
							0.132	0.121	0.011
							0.132	0.121	0.011
18	17	2	18	16	3	17.778453	0.073	0.069	0.004
							0.148	0.138	0.010
							0.148	0.138	0.010
20	18	2	20	17	3	11.065541	0.032	0.030	0.002
							0.065	0.060	0.005
							0.065	0.060	0.005
21	19	2	21	18	3	11.592719	0.045	0.044	0.001
							0.091	0.087	0.004
							0.091	0.087	0.004
22	20	2	22	19	3	12.299804	0.059	0.058	0.001
							0.119	0.115	0.004
							0.119	0.115	0.004
23	21	2	23	20	3	13.186345	0.081	0.071	0.010
							0.155	0.143	0.012
							0.155	0.143	0.012
24	22	2	24	21	3	14.245341	0.087	0.084	0.003
							0.176	0.169	0.007
							0.176	0.169	0.007
25	23	2	25	22	3	15.462669	0.094	0.096	−0.002
							0.191	0.192	−0.001
							0.191	0.192	−0.001
26	24	2	26	23	3	16.817381	0.104	0.106	−0.002
							0.212	0.212	0.000
							0.212	0.212	0.000

inclusion of the μ_c-transitions did not diminish the correlation. As these lines are measured with less accuracy, they were not included in the final analysis of Table 1. The rotational and centrifugal distortion constants derived from independent fittings to both Hamiltonians are given in Table 3. The fitted parameters are in the upper part, derived parameters below the line. The "determinable linear combinations" of the distortion parameters of sixth order are not included in Table 3 due to the large uncertainties. The fitted constants were used to predict the μ_c-transitions of Table 2.

Although the analysis predicts lines very precisely, it is still not satisfactory, as the *A*, *B*-correlation is unexplained and the precision of some centrifugal distortion constants is low.

The torsional splittings given in Table 4 were analysed by the internal axis method (IAM) [16] using a modified version of the program contrived by Woods [17–20].

Molecular parameters are:

a) $w_1(s)$, a Fourier coefficient [21]. It is a function of the reduced barrier s.

b) I_α, the moment of inertia of the methyl group.

c) λ_g, $g = a, b, c$, the direction cosines of the angles between the internal rotation axes and the principal axes of inertia. The λ_g are constrained by $\Sigma\,\lambda_g^2 = 1$.

A fit of $w_1(s)$, I_α, λ_a and λ_b diverged. The fits of $w_1(s)$ and I_α with fixed λ_a and λ_b, and of $w_1(s)$, λ_a and λ_b with fixed I_α converged. The first fit given in Table 5 with λ_a and λ_b calculated from the r_z-structure for a vector perpendicular to the plane of the three H-atoms (Table 5, column 3 of [9]) resulted in a rather low $I_\alpha = 3.006$ amuÅ^2. The two other fits

Table 5. Results from an IAM-analysis of the torsional splittings of 30 lines of Table 4. Single standard deviations in brackets, assumptions in square brackets. Fitted and assumed parameters in the first four lines. Derived parameters and those for comparison in the lower part (below the line). $\overline{\Delta\nu_{exp}}$: mean experimental splitting, σ: mean square deviation, $\lambda_{g\,nv}$: direction cosines of a normal vector perpendicular to the plane of the three H-atoms, $\lambda_{g\,ccm}$: direction cosines of a vector from the C-atom to the centre of mass of the three H-atoms. Derived from structures [4, 9].

$w_1(s)$	$-0.2399\,(15)\cdot 10^{-5}$	$-0.208\,(23)\cdot 10^{-5}$	$-0.209\,(23)\cdot 10^{-5}$
$\lvert\lambda_a\rvert$	[0.754]	0.769 (30)	0.763 (30)
$\lvert\lambda_b\rvert$	[0.542]	0.530 (8)	0.526 (8)
I_χ[amuÅ^2]	3.006 (25)	[3.146]	[3.174]
$\lvert(w_1(s), I_\chi)\rvert$	0.678	–	–
$\lvert(w_1(s), \measuredangle(a, i))\rvert$	–	0.993	0.993
$\overline{\Delta\nu_{exp}}$ [kHz]	141	141	141
σ [kHz]	7	7	7
$\lvert\lambda_c\rvert$	[0.371]	0.356 (68)	0.376 (67)
s	77.99 (6)	79.4 (10)	79.3 (11)
V_3 [cal/mole]	2955.9 (23)	2853 (37)	2826 (39)
F [GHz]	176.674	167.550	166.123
$\measuredangle(a, i)$ [°]	[41.06]	39.7 (26)	40.3 (26)
$\measuredangle(b, i)$ [°]	[57.17]	57.98 (52)	58.29 (51)
$\measuredangle(c, i)$ [°]	[68.23]	69.1 (42)	67.9 (41)
$\lvert\lambda_{a\,nv}\rvert$	[0.754]	0.754	0.757 (7)
$\lvert\lambda_{b\,nv}\rvert$	[0.542]	0.542	0.544 (10)
$\lvert\lambda_{c\,nv}\rvert$	[0.371]	0.371	0.363 (2)
$\lvert\lambda_{a\,ccm}\rvert$	0.745	0.745	0.730 (24)
$\lvert\lambda_{b\,ccm}\rvert$	0.558	0.558	0.604 (15)
$\lvert\lambda_{c\,ccm}\rvert$	0.364	0.364	0.320 (30)

for $w_1(s)$, λ_a and λ_b were made with assumed $I_\chi = 3.146$ amuÅ^2 from the r_z-structure given in [9] and $I_\chi = 3.174$ amuÅ^2 from an r_s-structure (Table 6a, column 1 of [4]).

For the last two calculations the direction cosines λ_g determined from the torsional splittings are nearer to the $\lambda_{g\,nv}$ of a normal vector (nv) perpendicular to the plane of the three H-atoms than to the $\lambda_{g\,ccm}$ of a vector (ccm) from the C-atom to the centre of mass of the three H-atoms.

Unfortunately this statement is weak considering the error limits. More work is necessary to prove that the internal rotation axis parallel to the internal angular momentum is perpendicular to the plane of the three H-atoms.

The s-values of this work are less than $s = 80.5$ of [4] Table 6b. This results from the better resolution of MWFT spectroscopy. With the last column of Table 5 a comparison with [4] is intended. From the remaining two columns based on the r_z-structure we favor the first because of the lower correlation and the higher precision of the constants. We think that the r_z-structure is presently the most elaborate determination.

We intended to improve the analysis by inclusion of forbidden transitions, but we could not find any clear patterns, because the forbidden transitions were overlayed by regular transitions.

Within the range of our MWFT spectrometer we do presently not see any possibility to gain more information.

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