The Microwave Spectra of m-Xylene and m-Xylene-d_{10}. Determination of the Low Methyl Internal Rotation Barrier

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Z. Naturforsch. **56 a,** 635–640 (2001); received August 29, 2001

The rotational spectra of m-xylene, $(CH_3)_2C_6H_4$, and of m-xylene-d_{10}, $(CD_3)_2C_6D_4$, have been recorded between 6 and 26.5 GHz using pulsed beam Fourier transform microwave spectroscopy. The clue for the assignment of the internal rotation multiplets was the inertial defect derived from the A_1A_1 species transitions.

The rotational constants for m-xylene and m-xylene-d_{10} are A = 3572.1117(1) MHz / 2896.1195(17) MHz, B = 1761.8621(1) MHz / 1446.0236(15) MHz, C =1197.3943(2) MHz / 988.2357(7) MHz, the barrier to internal rotation of the two methyl groups are V_3 = 53.7(16) J/mol / 39.8(5) J/mol, their moments of inertia were assumed to be $I_\alpha = 3.14\ u\text{Å}^2$ / $6.28\ u\text{Å}^2$.

Key words: Rotational Spectra; Low Methyl Internal Rotation Barriers; Two Top Molecules; Molecular Beam Fourier Transform Microwave Spectroscopy.

1. Introduction

Although microwave spectroscopy was applied to investigate the effects of methyl internal rotation in rotational spectra since a long time and a considerable information on internal rotation barriers and parameters was gathered [1 - 5], only recently the type of two methyl top low barrier molecules was investigated [6, 7]. As in the spectra of low threefold barriers V_3, the rotational lines are widely split and the assignment is a severe problem.

After the analysis of the microwave spectrum of 2,6-lutidine, $(CH_3)_2C_5H_3N$, [7], we selected m-xylene, $(CH_3)_2C_6H_4$. Its spectrum differs considerably from that of o-xylene, $(CH_3)_2C_6H_4$, which has a spectrum of a high barrier two top molecule [8].

Like for 2,6-lutidine, the configurational symmetry of m-xylene is C_{2v}. The two methyl groups are equivalent. The rotational levels may be classified by the invariance group of the hamiltonian $C_{3v}^- \otimes C_{3v}^+$ [1, 9, 10].

As the deuterated methyl groups CD_3 have a moment of inertia I_α around the internal rotation axis nearly twice of that of CH_3, and in consequence the internal rotation or torsion multiplets are narrower, we started our work with m-xylene-d_{10}. As we noticed later, the splittings are in the order of 400 MHz. So the internal rotation multiplets could not be detected easily.

As m-xylene is a commonly applied solvent, the knowledge of its rotational spectrum is useful for analytical purposes [11].

2. Experimental Details

For this study a molecular beam (MB) Fourier transform microwave (FTMW) spectrometer [11] proved very useful, as it suppresses by supersonic beam cooling the rotational spectra of energetically higher states. This reduces drastically the line density of the rotational spectrum.

We used a mixture of 0.5% m-xylene or m-xylene-d_{10} with argon at a backing pressure of approximately 50 kPa (0.5 bar). These substances were purchased from Aldrich, Steinheim, FRG, and Merck, Sharp and Dohme, Canada. In the Tables 1, 2, and 3 the frequencies of the transitions are given as the mean value of the Doppler doublet components.

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Table 1. Frequencies ν_{obs} of the observed rotational transitions of the A_1A_1 state of m-xylene-d$_{10}$. $\delta_{A_1A_1}$ observed minus calculated deviation from centrifugal distorted rotor and δ_{int} from internal rotation analysis.
$\Delta(A_1A_1\text{-}EE)$ splitting between the A_1A_1- and the EE-components, and $\delta\Delta$ observed minus calculated deviation for the $\Delta(A_1A_1\text{-}EE)$ value.

J	K_-	K_+	J'	K'_-	K'_+	ν_{obs} [GHz]	$\delta_{A_1A_1}$ [kHz]	δ_{int} [kHz]	$\Delta(A_1A_1\text{-}EE)$ [MHz]	$\delta\Delta$ [MHz]
3	1	3	2	0	2	7.803265	2	–20		
3	3	0	2	2	1	16.583481	–15	–31		
3	3	1	2	2	0	16.483107	7	1		
4	0	4	3	1	3	8.239730	–5	91	1377.612	–1.451
4	1	4	3	0	3	9.496302	3	38	–1024.818	–1.793
4	2	3	3	1	2	13.876359	11	–24		
4	2	3	4	1	4	7.994107	4	–15	–37.715	–3.357
5	0	5	4	1	4	10.528680	6	–69	954.636	–0.330
5	1	5	4	0	4	11.220038	–13	12	–955.060	–1.841
5	2	4	4	1	3	15.398344	–7	–5	–224.051	–0.907
5	2	4	5	1	5	9.269190	63	69	–289.471	7.713
6	1	6	5	0	5	13.027834	–1	7	–687.106	–2.025
6	0	6	5	1	5	12.681639	4	8	542.138	0.031
6	2	5	5	1	4	16.782621	9	3		
6	4	3	6	3	4	12.747278	–1	–10		
7	0	7	6	1	6	14.748308	4	0	262.953	0.012
7	1	7	6	0	6	14.910662	–1	–12	–408.496	–1.920
7	2	6	6	1	5	18.144814	–8	–3		
7	4	3	7	3	4	11.323398	7	–5		
8	0	8	7	1	7	16.767700	3	36	109.343	–0.431
8	1	8	7	0	7	16.840463	–1	–4	-218.605	–1.670
8	4	4	8	3	5	10.461511	–3	–2		
9	0	9	8	1	8	18.763473	3	–4	35.438	–0.685
9	1	9	8	0	8	18.795043	–2	2	–114.160	–1.413
10	0	10	9	1	9	20.748195	0	1	3.476	–0.841
10	1	10	9	0	9	20.761557	1	2	–61.902	–1.231
11	0	11	10	1	10	22.727991	–2	6		

Table 2. Frequencies ν_{obs} of the observed rotational transitions of the A_1A_1-state of m-xylene. $\delta_{A_1A_1}$ and δ_{int} see Table 1.

J	K_-	K_+	J'	K'_-	K'_+	ν_{obs} [GHz]	$\delta_{A_1A_1}$ [kHz]	δ_{int} [kHz]
2	1	2	1	0	1	7.286211	–1	1
2	2	0	1	1	1	12.964277	–2	2
2	2	1	1	1	0	12.279462	1	–1
3	0	3	2	1	2	7.030884	0	0
3	1	3	2	0	2	9.440884	1	0
3	2	1	2	1	2	16.925152	–0	1
3	2	2	3	1	3	8.414810	–0	0
4	0	4	3	1	3	10.001867	0	1
4	1	4	3	0	3	11.492789	1	0
4	2	3	4	1	4	9.662741	0	0
4	3	1	4	2	2	10.027402	0	0
4	3	2	4	2	3	11.383981	2	–2
4	4	1	4	3	2	15.303402	1	–1
4	4	5	4	1	4	12.769851	–0	1
5	1	4	5	0	5	8.532374	–0	0
5	1	5	4	0	4	13.584259	–1	0
5	2	4	5	1	5	11.218401	–1	1
5	3	2	5	2	3	9.269968	1	1
5	3	3	5	2	4	11.888433	0	0
5	4	1	5	3	2	14.944877	–1	1
6	1	5	6	0	6	11.202789	1	–1
6	2	5	6	1	6	13.043891	–0	–2
6	3	4	6	2	5	12.680597	–0	0
7	0	7	6	1	6	17.874531	0	0
7	1	6	7	0	7	13.961626	0	2
7	1	7	6	0	6	18.062938	0	0
7	2	5	6	3	4	15.013613	–0	2
7	2	6	7	1	7	15.084169	0	0
7	3	5	7	2	6	13.791970	–0	0
8	1	7	8	0	8	16.658458	–0	0
8	2	6	8	1	7	11.360978	–1	1
8	3	5	8	2	6	8.514478	–2	2
9	2	7	9	1	8	14.207691	3	–3
9	3	7	9	2	8	16.950123	0	0
9	4	5	9	3	6	11.533908	0	1
9	4	6	9	3	7	16.634037	–1	1
10	3	7	10	2	8	11.400744	0	0
10	4	6	10	3	7	10.929548	–1	1
11	4	7	11	3	8	11.002303	3	–3
12	3	9	12	2	10	16.968995	–1	1

3. Assignment and Analysis

3.1. m-xylene-d$_{10}$

As we could initially not identify internal rotation multiplets of rotational transitions of m-xylene, we searched for m-xylene-d$_{10}$ A_1A_1-species transitions, as they follow to second order perturbation theory the spectrum of a quasi rigid asymmetric rotor. The unresolved nuclear quadrupole hyperfine structure of the ten deuterium nuclei helped in the assignment of transitions with low rotational quantum number J. Their Doppler doublets appeared as unresolvable clusters of lines. As the hyperfine splitting decreases with increasing J the Doppler doublets become more clear with higher J. Figure 1 gives as an example transitions of the P-branch $J_{K_-K_+} - J'_{K'_-K'_+} = J_{1J} - (J-1)_{0\,J-1}$.

An extended search with the scanning mode of the MBFTMW spectrometer resulted finally in a complete assignment of the rotational spectrum in the A_1A_1-internal rotation state. The 27 measured lines are given in Table 1 column 2, the rotational and centrifugal distortion constants according Watson A-reduction [12] are given in Table 4, column 2.

We presented in [7] that, the inertial defect Δ beeing derived from rotational constants of the A_1A_1-species rotational spectrum of low barrier, two top molecules can be used to determine approximately the reduced barrier s,

$$s = \frac{4V_3}{9F}, \tag{1}$$

Table 3. Frequencies of the observed rotational transitions $\nu(\Gamma_i\Gamma_j)$ of the $\Gamma_i\Gamma_j = A_1E$-, EA_1- and EE-states of m-xylene and the difference $\Delta(A_1A_1\text{-}\Gamma_i\Gamma_j)$ of the A_1A_1-components of Table 2 and the A_1E-, EA_1- and EE-components $\nu(\Gamma_i\Gamma_j)$. $\delta\Delta$ observed minus calculated deviation for the $\Delta(A_1A_1\text{-}\Gamma_i\Gamma_j)$.

J	K_-	K_+	J'	K'_-	K'_+	$\Gamma_i\Gamma_j$	$\nu(\Gamma_i\Gamma_j)$ [GHz]	$\Delta(A_1A_1\text{-}\Gamma_i\Gamma_j)$ [MHz]	$\delta\Delta$ [MHz]
2	1	2	1	0	1	EE	7.130393	155.819	0.019
3	1	3	2	0	2	EE	10.366527	–925.642	–0.162
4	2	3	4	1	4	EE	9.763310	–100.569	0.073
4	4	1	4	3	2	A_1E	15.023667	279.735	–7.562
4	0	4	3	1	3	EE	8.290415	1711.452	–3.197
4	1	4	3	0	3	EE	12.752143	–1259.353	15.635
5	2	4	5	1	5	EE	11.624394	–405.993	–6.719
5	0	5	4	1	4	EE	11.590423	1179.428	–6.967
5	1	5	4	0	4	EA_1	14.113443	–529.184	2.376
6	2	5	6	1	6	EE	13.308342	–264.451	–5.363
6	0	6	5	1	5	EE	14.708152	665.576	–1.645
6	1	6	5	0	5	EE	16.625216	–846.730	5.447
7	1	6	7	0	7	EE	11.969434	2265.192	–13.693
7	2	6	7	1	7	EE	15.066911	17.258	–5.855
7	3	5	7	2	6	EE	14.108188	–316.218	–8.710
7	0	7	6	1	6	EA_1	17.932405	–57.874	–7.000
						EE	17.554621	319.910	–1.484
7	2	5	6	3	4	EA_1	14.987812	25.801	–1.787
8	2	6	8	1	7	EE	11.744257	–383.279	–2.346
8	0	8	7	1	7	EE	20.188065	131.294	–0.768
8	1	8	7	0	7	EE	20.670813	–267.638	–0.206
9	0	9	8	1	8	EE	22.695291	41.167	–0.622
9	1	9	8	0	8	EE	22.912188	–139.633	–0.382

and with the knowledge of the moment of inertia I_α the potential barrier V_3. F is the rotational constant of the internal rotation.

We followed the procedure given in [7]. In this paper the missprint in equation (4) should be changed to

$$F = \frac{\hbar^2}{2rI_\alpha}, \tag{2}$$

and equation (A.13) to

$$I_y - I_x - I_z = -2I_\alpha. \tag{3}$$

In Fig. 2 we give the dependence of the inertial defect Δ

$$\Delta = -2I_\alpha + 2W_{00}^{(2)}(s)\, I_\alpha \tag{4}$$

on the reduced barrier s for three assumed values for I_α. $\Delta = 0$ for $s = 0$, as $W_{00}^{(2)}(0) = 1$ and $\Delta < 0$ for $s > 0$, as $W_{00}^{(2)}(s) < 1$. $W_{v_i\sigma_i}^{(2)}(s), i = 1, 2$ is a second order perturbation coefficient tabulated for $s = 4$ to $s = 200$ by Hayashi and Pierce [13]. From $s = 0$ to $s = 4$ the coefficients were calculated in course of this work. v_i and σ_i designate the internal rotation state and substate. This allowed to estimate the reduced barrier s and an error range. The barrier parameters derived by this approximate method are given in Table 5, column 2.

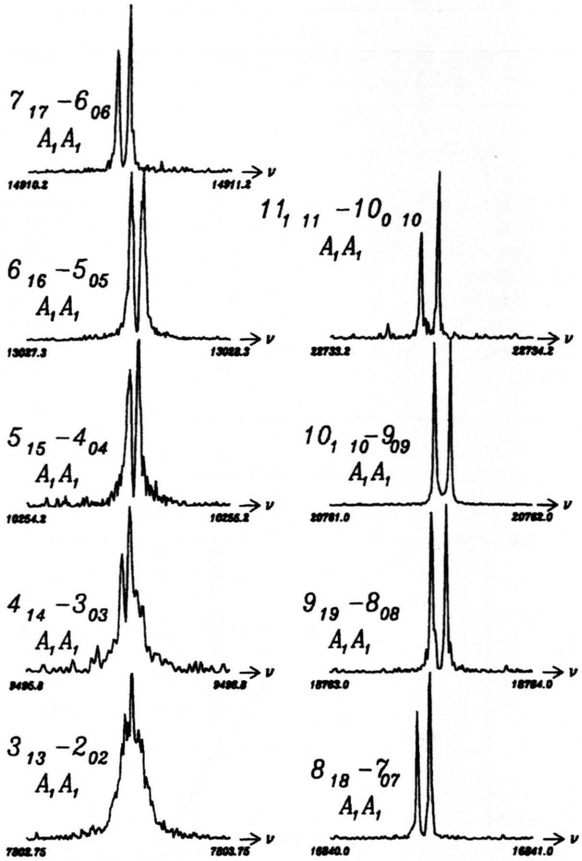

Fig. 1. The $J_{K-K+} - J'_{K'-K'+} = 3_{13} - 2_{02}$ to $11_{1,11} - 10_{0,10}$ rotational transitions of the A_1A_1-species of m-xylene-d$_{10}$. The lines are broadened by unresolveable hyperfine structure of ten deuterium nuclei. The broadening decreases with increasing J. The lines are split by the Doppler effect.

A consideration for the inertial defect to higher order will be given elsewhere [14].

To convert the equations of [7] we use the representation I^r [15] $x \leftrightarrow b, y \leftrightarrow c, z \leftrightarrow a$. For a prediction of the rotational transitions for the other internal rotation states, p. e. EE, the rotational constants A, B, C for a fictitious internal rotation free molecule must be determined. According (10) of [7] or [16] they are in approximation

Table 4. Rotational and centrifugal distortion constants (Watson A-Reduction [12]) of m-xylene and m-xylene-d_{10}, σ standard deviation and n number of lines of the A_1A_1 spectrum fitted as centrifugal distorted rotor columns 2 and 3 and fitted with the program TTWF columns 4 and 5. Precisely the rotational constants in columns 2 and 3 are $A_{A_1A_1}$ etc., of columns 4 and 5 structural rotational constants.

	m-xylene-d_{10}	m-xylene	m-xylene-d_{10}	m-xylene
A [MHZ]	3059.5069(18)	3694.0278(13)	2896.1195(17)	3572.1117(1)
B [MHZ]	1459.1068(14)	1771.6527(8)	1446.0236(15)	1761.8621(1)
C MHz]	988.2369(60)	1197.3946(7)	988.2357(7)	1197.3943(2)
Δ_J [kHz]	0.061(16)	0.0762(11)	0.054(18)	0.0778(4)
Δ_{JK} [kHz]	–0.122(50)	–0.1129(32)	–0.227(67)	–0.1324(19)
Δ_K [kHz]	1.331(128)	1.0355(120)	0.695(16)	0.9710(80)
δ_J [kHz]	0.021(76)	0.0277(16)	0.017(1)	0.0274(2)
Δ_K [kHz]	0.370(176)	0.1337(220)	0.368(196)	0.1228(22)
σ [kHz]	7	1	7.4	2.5
n	27	40	27	40

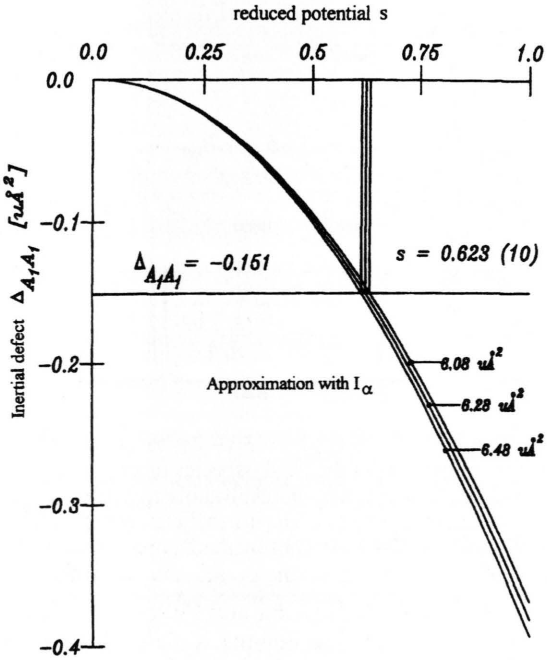

Fig. 2. Plot of the inertial defect Δ of m-xylene-d_{10} derived from the moments of inertia of the A_1A_1-species spectrum versus the reduced barrier s. Three values of I_α were assumed for an error estimate.

$$A = \frac{\hbar^2}{2I_a} = A_{A_1A_1} - 2W_{00}^{(2)}(s)\,\rho_a^2\,F, \tag{5}$$

$$B = \frac{\hbar^2}{2I_b} = B_{A_1A_1} - 2W_{00}^{(2)}(s)\,\rho_b^2\,F, \tag{6}$$

$$C = \frac{\hbar^2}{2I_c} = C_{A_1A_1}, \tag{7}$$

where A, B, C rotational constants of the internal rotation free molecule, structural rotational constants, I_a, I_b, I_c structural moments of inertia of the molecule, $A_{A_1A_1} = \overline{B}_a$, $B_{A_1A_1} = \overline{B}_b$, $C_{A_1A_1} = \overline{B}_c$ rotational constants of the $A_{A_1A_1}$-species lines [7], $W_{00}^{(2)}(s) = W_{v\sigma}^{(2)}(s)$ for $v = 0$ and $\sigma = 0$ second order perturbation coefficient, $\rho_g = \lambda_g I_\alpha / I_g$ for $g = a, b, c$, λ_g direction cosine between the internal rotation and principal inertia axes $g = a, b, c$, with $\lambda_c = 0$.

With knowledge of the structural rotational constants, the rotational constants $A_{\Gamma_1\Gamma_2}, B_{\Gamma_1\Gamma_2}, C_{\Gamma_1\Gamma_2}$ with $\Gamma_1\Gamma_2 = EE, A_1E, EA_1$ can be calculated. Therefore (5, 6) were rearranged and $2W_{00}^{(2)}(s)$ replaced by an appropriate choice of $W_{0\sigma_1}^{(2)}(s) + W_{0\sigma_2}^{(2)}(s)$. With these values a spectrum was predicted with the program TTWS, which uses the Hamiltonian and numerical procedure given in [17]. So we were able to assign the EE-species rotational transitions, which are the strongest components of the internal rotation multiplets. The internal rotation splittings $\Delta\nu = \nu_{A_1A_1} - \nu_{EE}$ and the A_1A_1-lines were analysed with the fitting program TTWF [17]. In columns 4 and 6 of Table 1 the residual fitting errors $\delta\nu_{\text{int}}$ and $\delta\Delta$ are listed. The determined rotational and centrifugal distortion constants are given in Table 4, column 4, the internal rotation parameters in Table 5, column 4.

3.2. m-xylene

For the assignment of the spectrum of m-xylene we used the information obtained from the spectrum of m-xylene-d_{10} in the following way.

With the program Gaussian 90 [18] we optimized the structure of m-xylene, as the deuterium is not included in the program. By substitution of deuterium

Table 5. Internal rotation parameters. I_α moment of inertia of the methyl group, α and β angles between the internal rotation axis and the principal inertia axes a and b, F internal rotational constant of the methyl top, Δ inertial defect, s reduced barrier, V_3 potential barrier, σ standard deviation, $\overline{\Delta}$ mean splitting, and n number of A_1A_1 lines or number of splittings. The parameters of column 2 and 3 were obtained by the analysis of the inertia defect as an estimate, of column 4 and 5 by complete internal rotation analysis of the multiplet spectrum.

	m-xylene-d$_{10}$	m-xylene	m-xylene-d$_{10}$	m-xylene
I_α [uÅ^2]	6.28*	3.14*	6.28*	3.14*
α [°]	30.00*	30.00*	30.1095(180)	30.2275(215)
β [°]	60.0*	60.0*	59.8905(180)	59.7725(215)
F [GHz]	78.252*	156.505*	83.132(45)	164.156(33)
Δ [uÅ^2]	−0.151	−0.00271		
s	0.623(10)	0.12(1)	0.533(7)	0.365(2)
V_3 [J/mol]	43.8(7)	16.9(2)	39.8(5)	53.7(16)
V_3 [cal/mol]	10.5(2)	4.04(5)	9.5(1)	12.8(4)
σ [MHz]			1.6	3.4
$\overline{\Delta}$ [MHz]			439	544
n	27	40	17	23

* assumed.

Table 6. Correlation and freedom-cofreedom matrices for m-xylene for the A_1A_1-spectrum fitted with the centrifugal distorted rotor model.

Correlations matrix

A	B	C	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K
1.000							
0.246	1.000						
0.343	0.825	1.000					
0.200	0.867	0.864	1.000				
0.192	0.160	−0.127	−0.034	1.000			
0.628	−0.284	−0.085	−0.216	−0.382	1.000		
−0.025	0.389	−0.138	0.102	0.616	−0.309	1.000	
−0.174	−0.198	0.101	0.014	−0.639	0.047	−0.769	1.000

Freedom-Cofreedom matrix F

A	B	C	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K
0.347							
0.984	0.181						
0.947	0.554	0.187					
0.986	0.698	0.698	0.410				
0.748	0.993	0.980	0.999	0.384			
0.560	0.979	0.978	0.987	0.700	0.326		
0.998	0.663	0.702	0.996	0.887	0.971	0.235	
0.961	0.911	0.871	0.997	0.823	0.945	0.649	0.406

in place of hydrogen in the optimized structure, the rotational constants of m-xylene-d$_{10}$ were calculated. Comparing these with the sightly different experimental rotational constants of Table 4, column 4, correction factors were obtained. The rotational constants of m-xylene, calculated with the optimized Gaussian 90 structure, were corrected. With (5 - 7) finally the rotational constants of the A_1A_1-species resulted. An approximated rotational spectrum could be predicted. With spectral scans the assignment of the A_1A_1-species lines could be completed. The following procedure for assigning transitions in other torsional substates was identical to that for m-xylene-d$_{10}$. The obtained frequencies are given in Tables 2 and 3. The rotational and centrifugal distortion constants are included in Table 4, column 5, the internal rotation parameters in Table 5, column 5. Typical correlation and freedom-cofreedom matrices [19] are reported in Table 6.

4. Discussion

It should be mentioned that the key for the assignment of the widely spaced internal rotation multiplets was the use of the inertial defect. From the inertial defect of the A_1A_1-lines and finally by the information given by the $A_1A_1 - EE$-splittings, the barrier parameters V_3, s, F, λ_a, and λ_b could be determined successively for m-xylene-d$_{10}$ by assumption of I_α.

The assignment and analysis of the spectrum of m-xylene with even wider multiplets followed the same procedure using the information from m-xylene-d$_{10}$.

We have shown that the potential barrier can be successfully obtained in approximation via the inertial defect in the case of a small potential barrier. But the information from the multiplet splittings is still necessary for a more precise determination.

In the case of high barriers, the V_3-potential values of deuterated methyl groups are by about 10% less than those for normal isotopomers [20]. Surprisingly, the potential barrier of m-xylene-d$_{10}$ is by about 25% smaller than that of m-xylene.

Acknowledgement

We thank the members of our group for help and discussion. Financial support from the Bundesministerium für Forschung und Technologie, the Deutsche Forschungsgemeinschaft, the Fonds der Chemie, and the Land Schleswig-Holstein is gratefully acknowledged. The calculations were carried out at the computer center of the University of Kiel.

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