Reanalysis of the Nuclear Quadrupole Coupling in the Rotational Spectrum of N-Methylpyrrole

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The rotational spectrum of N-methylpyrrole has been measured with pulsed nozzle Fourier transform microwave spectrometers between 6 and 38 GHz. The quadrupole hyperfine structure due to ^{14}N has been reanalyzed in the A $(m = 0)$ state of the methyl internal rotation. Improved rotational constants, centrifugal distortion constants, and quadrupole coupling constants have been simultaneously determined from the measured transition frequencies in an iterative least-squares fit.

Introduction

The rotational spectrum of N-methylpyrrole ($C_4H_4NCH_3$) was investigated some time ago by Arnold *et al.* [1] using conventional Stark spectroscopy. The spectrum showed typical effects of the internal rotation of the methyl group hindered by a small sixfold barrier. Each rotational transition was further split by the nuclear quadrupole interaction due to ^{14}N. The analysis of the measured rotational transitions yielded rotational constants, quadrupole coupling constants, and internal rotation parameters [1].

Recently, the rotational spectrum of the N-methylpyrrole–argon complex has been studied in Zürich [2]. When the quadrupole coupling constants of N-methylpyrrole given in [1] were transformed to the principal axis system of the complex, it was noticed that their values disagreed substantially from those obtained in the analysis of the complex. The former values also deviated largely from the quadrupole coupling constants of pyrrole [3]. A check of the quadrupole splitting patterns for a few rotational transitions in the A $(m = 0)$ internal rotation state using a pulsed nozzle Fourier transform microwave (FTMW) spectrometer revealed that the quadrupole coupling constants needed a revision.

The results of a reinvestigation of the rotational spectrum for N-methylpyrrole are presented here. The measurements were performed in the laboratories of Zürich and Kiel using pulsed nozzle FTMW spectrometers. A comparison of measured transition frequencies from both laboratories provide an estimate of the accessible accuracy. It should be pointed out again that the determination of the frequencies in a narrow multiplet must be handled with care [4–6].

Experimental

N-methylpyrrole (Aldrich) was used as received without further purification or distilled once. A detailed description of the pulsed nozzle FTMW spectrometers with a design similar to that of Balle and Flygare [7] was given elsewhere [8–12].

In Zürich, all measurements were performed by expanding a gas mixture of 0.5% N-methylpyrrole in argon at a backing pressure of 100 kPa through a nozzle of 0.5 mm diameter perpendicular to the cavity axis. The molecules were polarized with microwave pulses of 1 μs duration and a power of 0.4 mW. Two to four microwave pulses were applied to a single gas pulse. The polarization decays were sampled with a 12-bit analog-to-digital converter for 512 or 1024 channels. Adequate signal-to-noise ratios were obtained by adding the polarization decays from 50 gas pulses for the stronger transitions and for up to

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Table 1. Observed hyperfine components of N-methylpyrrole. Their frequencies ν_{obs} are given as mean values of Zürich and Kiel measurements (column 5). In column 6, the difference δ between the measurements in Kiel and Zürich are given. Values taken only in Kiel or in Zürich are marked by a "K" or a "Z" in the same column. The last column presents the deviation between experimental and theoretical frequencies calculated with the values of Table 2.

J'–J^{a}	F'-F	ν_{obs} [MHz]	δ [KHz]	ν_{calc} [MHz]	$\Delta\nu^{\text{b}}$ [MHz]
1_{01}–0_{00}	0–1	6125.9613	K	6125.9599	0.0014
	2–1	6126.7811	K	6126.7816	−0.0005
	1–1	6127.3303	K	6127.3294	0.0009
4_{13}–4_{14}	4–4	9864.7073	−2.0	9864.7090	−0.0017
	5–5	9866.0309	1.4	9866.0322	−0.0013
	3–3	9866.3703	−0.1	9866.3725	−0.0022
7_{25}–7_{26}	7–7	10839.2343	K	10839.2369	−0.0026
	8–8	10840.0461	K	10840.0437	0.0024
	6–6	10840.1580	K	10840.1600	−0.0020
2_{12}–1_{11}	1–1	11259.7646	0.0	11259.7631	0.0015
	1–2	11260.0791	Z	11260.0819	−0.0028
	3–2	11260.6016	−0.8	11260.5977	0.0039
	2–1	11261.2098	−0.7	11261.2075	0.0023
	2–2	11261.5264	−1.5	11261.5263	0.0001
2_{02}–1_{01}	1–1	12132.1499	−1.0	12132.1486	0.0013
	3–2	12133.0782	−0.7	12133.0761	0.0021
	2–1	12133.2114	5.8	12133.2119	−0.0005
	1–0	12133.5162	−3.1	12133.5181	−0.0019
	2–2	12133.7602	−0.7	12133.7597	0.0005
2_{11}–1_{10}	1–0	13245.5401	−0.9	13245.5385	0.0016
	2–2	13246.3058	2.9	13246.3070	−0.0012
	3–2	13246.6496	−0.4	13246.6486	0.0010
	2–1	13247.1738	−1.3	13247.1736	0.0002
	1–1	13247.7050	−1.3	13247.7052	−0.0002
5_{14}–5_{15}	5–5	14641.5069	0.9	14641.5053	0.0016
	6–6	14642.8111	−1.6	14642.8100	0.0011
	4–4	14643.0796	0.1	14643.0758	0.0038
3_{13}–2_{12}	2–2	16818.4167	−0.3	16818.4142	0.0025
	4–3	16819.7467	−1.7	16819.7431	0.0036
	2–1	16819.8560	4.1	16819.8586	−0.0026
	3–2	16819.9606	1.3	16819.9586	0.0020
	3–3	16820.8880	−2.4	16820.8872	0.0008
3_{03}–2_{02}	2–2	17908.5021	2.2	17908.5048	−0.0027
	4–3	17909.4854	−1.3	17909.4859	−0.0005
	2–1	17909.5683	−3.4	17909.5681	0.0002
	3–2	17909.6535	−3.9	17909.6526	0.0009
	3–3	17910.3346	1.2	17910.3361	−0.0015
3_{22}–2_{21}	2–1	18380.1007	−0.6	18380.1025	−0.0018
	4–3	18380.4278	−3.0	18380.4286	−0.0008
	3–2	18381.0151	−0.5	18381.0156	−0.0005
3_{21}–2_{20}	2–1	18851.2208	4.6	18851.2224	−0.0016
	4–3	18851.5160	−0.2	18851.5176	−0.0016
	3–2	18851.9599	2.2	18851.9597	0.0002
3_{12}–2_{11}	4–3	19789.4928	0.0	19789.4920	0.0008
	3–2	19789.6661	1.3	19789.6660	0.0001
4_{14}–3_{13}	5–4	22305.4762	−0.6	22305.4729	0.0033
	3–2	22305.5499	K	22305.5460	0.0039
	4–3	22305.6029	K	22305.6016	0.0013
	4–4	22306.7485	Z	22306.7456	0.0029
	3–3	22304.0029	Z	22304.0016	0.0013
4_{04}–3_{03}	4–3	23395.3257	K	23395.3294	−0.0037
	5–4	23395.1398	K	23395.1450	−0.0052
	3–2	23395.1747	K	23395.1765	−0.0018
	4–4	23396.1736	0.2	23396.1796	−0.0060
	3–3	23394.0235	−0.1	23394.0288	−0.0053
4_{23}–3_{22}	4–3	24413.4451	K	24413.4418	0.0033
	3–2	24413.1050	K	24413.0985	0.0065
	5–4	24413.1710	K	24413.1687	0.0023
6_{16}–5_{15}	7–6	33041.7151	K	33041.7163	−0.0012
	5–4	33041.7496	K	33041.7504	−0.0008
	6–5	33041.7955	K	33041.7972	−0.0017
6_{34}–5_{33}	5–4	37197.7498	K	37197.7502	−0.0004
	7–6	37197.7765	K	37197.7765	0.0000
	6–5	37197.9273	K	37197.9254	0.0019
5_{15}–4_{14}	6–5	27711.4114	K	27711.4097	0.0017
	4–3	27711.4592	K	27711.4579	0.0013
	5–4	27711.5081	K	27711.5069	0.0012
	4–4	27709.8587	K	27709.8579	0.0008
	5–5	27712.7799	K	27712.7797	0.0002
5_{32}–4_{31}	4–3	31148.5987	K	31148.6040	−0.0053
	6–5	31148.6592	K	31148.6644	−0.0052
	5–4	31148.8738	K	31148.8790	−0.0052
6_{33}–5_{32}	5–4	37679.5507	K	37679.5467	0.0040
	7–6	37679.5657	K	37679.5640	0.0017
	6–5	37679.6477	K	37679.6460	0.0017

[a] $J'_{K'_-K'_+}$–$J_{K_-K_+}$, [b] $\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$.

Table 2. Rotational, centrifugal distortion[a] and quadrupole coupling constants of N-methylpyrrole in the A $(m = 0)$ state of the methyl internal rotation with standard errors given in units of the last digit in brackets. A_{eff}: the effective rotational constant of the A state; σ: the standard deviation of a single transition; N: the number of analyzed components.

Constant	Kiel and Zürich	Kiel	Zürich
A_{eff}/MHz	9165.0574(41)	9165.0560(41)	9165.016(17)
B/MHz	3559.92967(19)	3559.92969(20)	3559.92946(37)
C/MHz	2566.94415(13)	2566.94411(13)	2566.94495(31)
Δ_J/kHz	0.2292(26)	0.2295(26)	0.222(13)
Δ_{JK}/kHz	1.569(14)	1.566(14)	1.772(97)
δ_j/kHz	0.0763(20)	0.0769(20)	0.0648(63)
χ_{aa}/MHz	1.8261(18)	1.8255(19)	1.8261(21)
χ_{bb}/MHz	1.0628(23)	1.0626(23)	1.0631(26)
χ_{cc}/MHz	−2.8889(16)	−2.8881(17)	−2.8892(18)
σ/kHz	2.65	2.59	2.48
N	75	72	44

[a] Centrifugal distortion constants according to the definition of Watson [15].

1000 gas pulses for the weakest transitions. The center frequencies of the quadrupole components were determined by fits in the frequency domain with a Lorentzian line shape [13].

In Kiel, a gas mixture with a backing pressure of 50 kPa was prepared which contained 1% N-methylpyrrole in argon. The nozzle was placed near the center of one of the two mirrors forming the cavity which produced a molecular beam propagating parallel to the cavity axis. The optimization of the $\pi/2$–condition led to microwave pulses of 0.5 μs duration with a power of 0.4 mW. The pulse-controlling electronic equipment at Kiel allowed for one microwave pulse per gas pulse. For the stronger transitions, 128 experiment cycles resulted in recordings with sufficient signal-to-noise ratio. Up to 4096 cycles were required for a few of the weaker transitions in the Q-branch with J-values up to 7. The frequencies of narrowly split transitions were determined by a program based on the fitting of the time domain signal [6].

Results and Analysis

The measured frequencies for the quadrupole components of the observed rotational transitions are listed in Table 1. If the frequencies were measured in both laboratories, their arithmetic mean is given together with the difference between the values from Kiel and Zürich. Otherwise, the measured frequency is marked with a label indicating the laboratory from which it originated.

The frequencies of the rotational transitions in the A $(m = 0)$ state of the internal rotation with a low sixfold barrier as in N-methylpyrrole match those of a rigid asymmetric rotor. The rotational constant A is replaced by an effective rotational constant A_{eff} which is given by the expression

$$A_{\text{eff}} = \frac{h}{8\pi^2\,(I_a - I_\alpha)} \;, \tag{1}$$

where I_a is the moment of inertia of the whole molecule about the principal axis a which coincides with the internal rotation axis and I_α represents the moment of inertia of the methyl group, see [1]. Because the rotational transitions of exclusively the A state were remeasured the model of an asymmetric rotor with hyperfine splittings was sufficient for their analysis.

Rotational constants, centrifugal distortion constants and quadrupole coupling constants were simultaneously determined from the measured frequencies in Table 1 in an iterative least-squares fit. The program of Pickett [14] for an asymmetric top with hyperfine splittings was used which diagonalized the complete Hamiltonian matrix. The centrifugal distortion constants were defined according to Watson's asymmetric reduction in the prolate I^{r} representation [15]. Because of the symmetry of N-methylpyrrole which exclusively allowed the observation of μ_a-type transitions and because of the limited range of observable J-values up to 7 due to the strong cooling in the nozzle, only three centrifugal distortion constants were determinable. The least-well determined constants Δ_K and δ_K were constrained to zero. The results of the fit are given in the first column of Table 2. Identical results were obtained in Kiel with the program HFS [16] for which the centrifugal distortion constants are defined according to the reduction given by van Eijck [17].

Discussion and Conclusions

The quadrupole coupling constants of N-methylpyrrole given in Table 2 are compared to those of pyrrole [3]:

$$\begin{aligned}\chi_{aa} &= 1.45(2)\text{ MHz},\\ \chi_{bb} &= 1.21(2)\text{ MHz},\\ \chi_{cc} &= -2.66(2)\text{ MHz}.\end{aligned}$$

The component χ_{cc} perpendicular to the aromatic ring plane agrees reasonably between the two molecules. The other two components show larger deviations reflecting the different electron distribution originating in the attached hydrogen or methyl group. If the quadrupole coupling constants of Table 2 were transformed to the principal axis system of the N-methylpyrrole–argon complex they were compatible with those measured for the complex [2].

The mean residual deviation of a measured frequency from that calculated with the constants of Table 2 amounts to 2.65 kHz which is compatible with the mean absolute difference of 1.52 kHz between the frequencies measured in Kiel and Zürich. Measurements taken in Kiel with two different spectrometers covering about the same range of frequencies [9-11] showed only a mean absolute difference of about 0.7 kHz. The mean absolute difference of the frequencies obtained in two laboratories provides a useful measure of the precision for the frequency measurements of rotational transitions with narrowly split multiplets. Individual fits of the frequencies measured in Kiel or of those in Zürich are included in Table 2 for comparison. The rotational constants, the quadrupole coupling constants and the mean residual deviations agree very well among the three fits. However, the smaller data set of Zürich produced centrifugal distortion constants which differ by more than the combined standard deviations from the other two fits.

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