The Microwave Spectrum of 4-Methylisoxazole: ^{14}N Nuclear Quadrupole Coupling, Methyl Internal Rotation and Electric Dipole Moment

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The microwave spectrum of 4-methylisoxazole has been investigated in the frequency range from 8 to 40 GHz, employing both Stark and Fourier transform spectroscopy. We present the results from a ^{14}N quadrupole hyperfine structure, a fourth-order centrifugal distortion and an IAM methyl internal rotation analysis. The components of the electric dipole moment with respect to the principal axes of inertia have been obtained from the Stark splittings of some rotational lines.

Introduction

Some years ago the five-membered heterocyclic ring compounds oxazole and isoxazole have been studied in great detail by microwave spectroscopy, in particular to obtain information on the ^{14}N nuclear quadrupole coupling tensor [1, 2]. More recently these studies were extended to the three isomeric monomethyl derivatives of oxazole [3] and the monomethyl derivatives of isoxazole at the 3- and 5-position of the heterocyclic ring [4]. The objective of these investigations was mainly to examine the influence of methyl substitution on the ^{14}N nuclear quadrupole coupling tensor and on the barrier height of the potential hindering methyl internal rotation. The same questioning was motivating for the present work on 4-methylisoxazole, which completes these earlier studies.

Experimental

The rotational spectrum of 4-methylisoxazole was first investigated and assigned at Bangor, using a conventional 100 kHz Stark effect modulated spectrometer in the frequency range from about 16 to 40 GHz at sample pressures down to a few mTorr and at ambient temperatures. Though the rotational lines were sufficiently split due to methyl internal rotation for many transitions, the ^{14}N nuclear quadrupole hyperfine structure (hfs) was not well resolved in these studies. Therefore the measurements were resumed at Kiel, taking advantage of the improvements in both resolution and sensitivity by the Fourier transform technique in microwave spectroscopy. Microwave Fourier transform (MWFT) spectrometers in X- [5], Ku- [6] and K-band [7], i.e. from 8 to 26 GHz, were used for the measurements at sample pressures below 1 mTorr and at temperatures of about −70 °C. The fine and hyperfine structure analyses reported here are based on these recordings by MWFT-spectroscopy.

The electric dipole moment was determined from the Stark splittings of rotational lines in V-band, i.e. from 26 to 40 GHz, at Kiel, using a conventional Stark spectrometer with 100 kHz modulation frequency. The sample was prepared in the Institut für Organische Chemie der Universität Kiel and used without further purification.

Analysis

The analysis of the spectrum was carried out in an approximate way considering the perturbations

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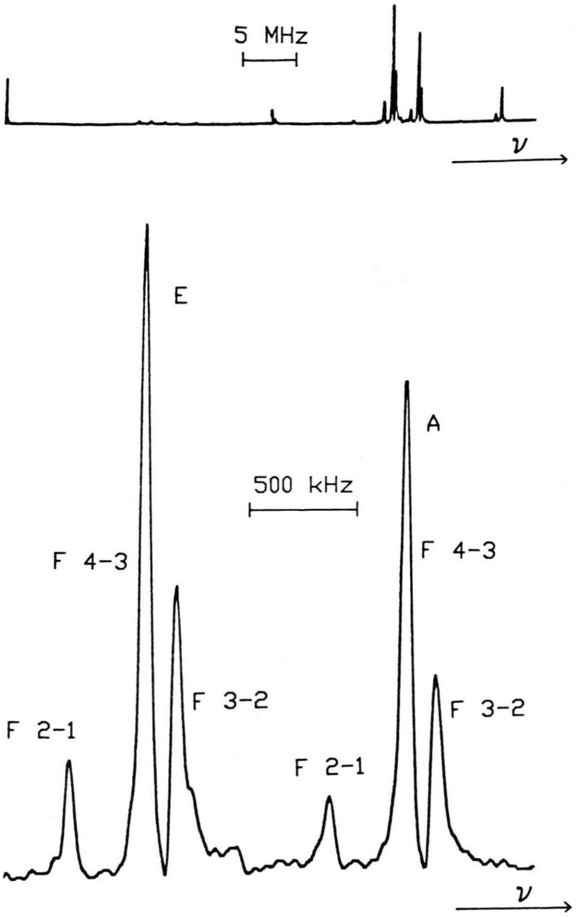

Fig. 1. *Upper trace:* A 50-MHz scan of the rotational spectrum of 4-methylisoxazole. Transition $J'(K'_-, K'_+) - J''(K''_-, K''_+) = 3(0,3) - 2(0,2)$; power spectrum; sample interval: 10 nsec; averaging cycles: 960 K; 1024 data points; polarizing frequency: 16358.0 MHz; pressure: 2 mTorr; temperature: -20 °C. *Lower trace:* A range of 2.5 MHz of the upper trace.

from ^{14}N nuclear quadrupole coupling, centrifugal distortion and methyl internal rotation as independent contributions to the rigid rotor hamiltonian. In accord with these assumptions the A- and E-species components of the torsional doublet of a rotational line do not exhibit significantly different ^{14}N-hfs patterns. Therefore the ^{14}N-hfs analysis was carried out only for the A-lines, using a first order perturbation treatment of nuclear quadrupole coupling to yield the coupling constants $\chi_+ = \chi_{bb} + \chi_{cc}$ and $\chi_- = \chi_{bb} - \chi_{cc}$ [8].

In the next step of the analysis these coupling constants were used to calculate the splittings relative to a single rigid rotor line and to correct the experimental hfs components with these splittings. With the arithmetic mean value of the resultant frequencies, hypothetical unsplit lines ν^0 were obtained and used as a basis for the centrifugal distortion and internal rotation analyses. The centrifugal distortion analysis was based on the Hamiltonian according to Watson's S-reduction [9] and was carried out only for the A-species lines because of their pseudo-rigid rotor behaviour. As result of a least squares analysis of all transitions, measured in Bangor and Kiel, the rotational constants A, B and C and the five fourth-order centrifugal parameters D_J, D_{JK}, D_K, d_1 and d_2 were obtained.

The internal rotation IAM analysis was based on the splittings $\nu_A^0 - \nu_E^0$ of the hypothetical unsplit A- and E-lines and was performed with a program written by Woods [10, 11] modified in Kiel *. As result of a least squares analysis all internal rotation parameters, i.e. the Fourier coefficient $w_1(s)$ and therewith the reduced barrier height s, the angle between the principal inertia axis a and the internal rotation axis $i \sphericalangle (a, i)$, and the moment of inertia of the methyl group I_α could be determined.

The electric dipole moment of 4-methylisoxazole was determined from the Stark splittings of the transitions $J(K_-, K_+) = 6(0,6) - 5(0,5)$, $6(2,5) - 6(2,4)$, $7(0,7) - 6(0,6)$ and $7(1,7) - 6(1,6)$ at field strengths of about 1000 to 2000 V/cm. Transitions with lower J-quantum number could not be investigated because of the limited sensitivity of the Stark spectrometer.

Results and Discussion

A total of 71 a- and b-type rotational transitions up to a maximum J-value of 39 have been observed and used for the present analysis. The frequencies of narrowly split lines were obtained by comparing experimental with simulated lineshapes. Some low J-lines are listed in Table 1, including ^{14}N-hfs and A-E splittings. A complete list is available under No. TNA3 (W. Jäger, H. Dreizler, H. Mäder) from the Universitätsbibliothek, University of Kiel.

In order to demonstrate the resolution and the signal to noise ratio as achieved by MWFT spectroscopy the recording of the transition $J(K_-, K_+) = 3(0,3) - 2(0,2)$ is shown in Fig. 1 as an example.

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* Program AC3IAM, modified by W. Kasten.

Table 1. Measured transitions of 4-methylisoxazole. Γ: symmetry species; ν_{obs}: observed frequency; ν_A^0, ν_E^0: hypothetical centre line frequencies of A- respectively E-species extrapolated from measured hfs-component frequencies with calculated hfs-splittings; ν_A^0 (calc), ν_E^0 (calc): hypothetical centre line frequencies obtained by centrifugal distortion calculations respectively methyl internal rotation calculations. Frequencies in MHz.

$J'(K'_-, K'_+) - J''(K''_-, K''_+)$	$F' - F''$	Γ	ν_{obs}	ν_A^0	ν_A^0 (calc)	ν_E^0	ν_E^0 (calc)
2 (1, 2) − 1 (1, 1)				10 939.259	10 939.260		
	3 − 2	A	10 939.505				
	2 − 1	A	10 938.002				
3 (2, 1) − 2 (2, 0)				18 104.508	18 104.502		
	4 − 3	A	18 104.916				
	3 − 2	A	18 103.106				
	2 − 1	A	18 105.868				
3 (0, 3) − 2 (0, 2)				17 363.880	17 363.882	17 362.656	17 362.648
	4 − 3	A	17 363.892				
		E	17 362.661				
	3 − 2	A	17 364.020				
		E	17 362.806				
	2 − 1	A	17 363.530				
		E	17 362.305				
3 (1, 3) − 2 (1, 2)				16 352.782	16 352.776	16 360.046	16 359.925
	4 − 3	A	16 352.875				
		E	16 360.139				
	3 − 2	A	16 352.468				
		E	16 359.745				
	2 − 1	A	16 353.038				
		E	16 360.288				
3 (2, 2) − 2 (2, 1)				17 734.170	17 734.169	17 861.742	17 861.323
	4 − 3	A	17 734.531				
		E	17 862.116				
	3 − 2	A	17 732.905				
		E	17 860.469				
	2 − 1	A	17 735.436				
		E	17 863.001				
3 (2, 2) − 3 (1, 3)				21 259.424	21 259.411		
	4 − 4	A	21 259.328				
	3 − 3	A	21 259.739				
	2 − 2	A	21 259.164				
3 (1, 3) − 2 (0, 2)				21 306.073	21 306.058		
	4 − 3	A	21 305.837				
	3 − 2	A	21 306.946				
	2 − 1	A	21 305.142				
4 (1, 3) − 4 (1, 4)				8 791.421	8 791.427		
	5 − 5	A	8 791.868				
	4 − 4	A	8 790.232				
	3 − 3	A	8 792.255				
4 (2, 2) − 3 (2, 1)				24 456.445	24 456.445	24 337.931	24 337.732
	5 − 4	A	24 456.691				
		E	24 338.182				
	4 − 3	A	24 455.806				
		E	24 337.256				
	3 − 2	A	24 456.876				
		E	24 338.392				
4 (0, 4) − 3 (0, 3)				22 760.767	22 760.759	22 758.070	22 758.170
	5 − 4	A	22 760.737				
		E	22 758.043				
	4 − 3	A	22 760.923				
		E	22 758.231				
	3 − 2	A	22 760.570				
		E	22 757.867				

Table 1 (continued)

$J'(K'_-, K'_+) - J''(K''_-, K''_+)$	$F' - F''$	Γ	ν_{obs}	ν_{A}^0	ν_{A}^0 (calc)	ν_{E}^0	ν_{E}^0 (calc)
4 (3, 1) − 3 (3, 0)				23 854.277	23 854.272	23 834.957	23 834.792
	5 − 4	A	23 854.663				
		E	23 835.349				
	4 − 3	A	23 853.089				
		E	23 833.796				
	3 − 2	A	23 855.258				
		E	23 853.906				
4 (1, 3) − 3 (1, 2)				25 203.852	25 203.849	25 200.152	25 199.970
	5 − 4	A	25 203.913				
		E	25 200.218				
	4 − 3	A	25 203.782				
		E	25 200.080				
	3 − 2	A	25 203.782				
		E	25 200.080				
4 (1, 4) − 3 (1, 3)				21 707.396	21 707.394	21 709.884	21 709.757
	5 − 4	A	21 707.437				
		E	21 709.925				
	4 − 3	A	21 707.304				
		E	21 709.793				
	3 − 2	A	21 707.437				
		E	21 709.925				
5 (1, 4) − 5 (1, 5)				13 079.176	13 079.180	13 084.146	13 083.879
	6 − 6	A	13 079.631				
		E	13 084.599				
	5 − 5	A	13 078.007				
		E	13 082.984				
	4 − 4	A	13 079.950				
		E	13 084.916				

Table 2. ^{14}N Quadrupole coupling constants of 4-methylisoxazole. χ_+, χ_-: Quadrupole coupling constants ($\chi_+ = \chi_{bb} + \chi_{cc}$ and $\chi_- = \chi_{bb} - \chi_{cc}$); σ: standard deviation of the fit; $\overline{\Delta\nu}_{\mathrm{exp}}$: mean experimental hfs-splitting; standard errors in brackets.

		Correlation matrix	
$\overline{\Delta\nu}_{\mathrm{exp}}$	5.0616(18) MHz	1.000	
χ_+	4.8654(15) MHz	0.004	1.000
χ_-	0.014 MHz		
σ	0.609 MHz		
χ_{aa}	−5.0616(18) MHz		
χ_{bb}	4.9635(17) MHz		
χ_{cc}	0.0981(17) MHz		

The results for the quadrupole coupling constants χ_{gg} ($g = a, b, c$) from the ^{14}N-hfs analysis of 43 A-lines are given in Table 2. No value for the off-diagonal tensor element χ_{ab} could be evaluated from our data and hence the principal components of the χ-tensor could not be determined. However, comparing the fitted coupling constants with its estimates, initially calculated to facilitate the assignment of lines, indicates that the position of principal axes of the coupling tensor with respect to the isoxazole ring is not much changed upon methyl substitution. These estimates were obtained as $\chi_{aa} = -5.10$ MHz, $\chi_{bb} = 5.02$ MHz, $\chi_{cc} = 0.08$ MHz and $\chi_{ab} = -1.82$ MHz, using the principal components of the χ-tensor and its orientation in isoxazole [12] and assuming the r_s-structure of isoxazole [13] together with a plausible methyl structure (C−C-distance = 1.52 Å; C−H-distance = 1.10 Å; C−C−H-angle = tetrahedral angle; C−C−CH$_3$-angle = C−C−H-angle in isoxazole) for determination of the angle $\sphericalangle (x, a)$ between the principal coupling tensor x-axis and the principal inertial a-axis of 4-methyl-isoxazole (see Figure 2).

The results from the centrifugal distortion analysis including the A-lines up to $J = 27$ are given in Table 3 and were used to predict line center frequencies of transitions involving higher J quantum numbers.

The rotational constant A and the centrifugal distortion constant D_K are less accurately determined since only a few b-type lines which contain more information about these constants could be measured because of their low intensity.

Table 3. Rotational and centrifugal distortion constants of 4-methylisoxazole. A, B, C: rotational constants; D_J, D_{JK}, D_K, d_1, d_2: fourth order centrifugal distortion constants according to Watson's S-reduction; σ: standard deviation of the fit; standard errors in brackets.

		Correlation matrix							
A	9140.0318(21) MHz	1.000							
B	3397.4849(9) MHz	0.449	1.000						
C	2513.9304(9) MHz	0.306	0.958	1.000					
D_J	0.2441(129) kHz	0.339	0.909	0.921	1.000				
D_{JK}	2.0231(283) kHz	0.139	0.208	0.067	0.077	1.000			
D_K	16.5513(2300) kHz	0.069	−0.181	−0.096	−0.083	−0.961	1.000		
d_1	−0.0652(8) kHz	−0.103	−0.226	−0.028	−0.079	−0.823	0.731	1.000	
d_2	−0.0111(4) kHz	−0.057	0.203	0.048	0.086	0.747	−0.703	−0.969	1.000
σ	0.015 MHz								

Table 4. Internal rotation parameters of 4-methylisoxazole. $w_1(s)$: first Fourier coefficient; I_α: moment of inertia of the methyl group; $\sphericalangle(i, a)$: angle between the internal rotation axis i and the principal inertia axis a; s: reduced barrier height; V_3: potential coefficient; F: reduced rotational constant; σ: standard deviation of the fit; $\overline{\Delta\nu_{AE}}$: mean experimental splitting; standard errors in brackets.

		Correlation matrix		
$w_1(s)$	$-0.50948(67) \cdot 10^{-2}$	1.000		
I_α	3.091(16) amuÅ^2	−0.210	1.000	
$\sphericalangle(i, a)$	6.9(4)°	−0.675	0.839	1.000
s	19.9004(59)			
V_3	738.9(43) cal/mol			
V_3	3.093(180) kJ/mol			
F	173.0(9) GHz			
σ	0.220 MHz			
$\overline{\Delta\nu_{AE}}$	42.463 MHz			

Table 5. Dipole moment components of 4-methylisoxazole. μ_a, μ_b: dipole moment components in direction of the principal inertia axes a and b; μ_{total}: total dipole moment; σ: standard deviation of the fit; $\overline{\Delta\nu_{exp}}$: mean experimental splitting; standard errors in brackets.

		Correlation matrix	
μ_a	3.545(5) D	1.000	
μ_b	0.522(4) D	−0.674	1.000
μ_{total}	3.583(5) D		
σ	0.067 MHz		
$\overline{\Delta\nu_{exp}}$	5.422 MHz		

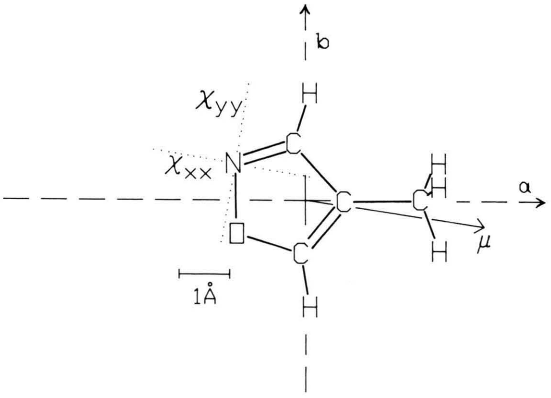

Fig. 2. Alignment of the principal inertia axes a and b, the dipole moment vector and the ^{14}N nuclear quadrupole coupling tensor in 4-methylisoxazole. ------ principal inertia axes under the mentioned assumptions; ······ nuclear quadrupole coupling tensor axes; —— most probable alignment of the dipole moment vector.

To obtain the fit parameters of the IAM methyl internal rotation analysis given in Table 4, only the A-E splittings of a-type lines up to $J = 19$ were taken into account. Inclusion of A-E splittings of b-type lines and/or lines with higher J quantum numbers made the fit considerably worse, most probably because of approximations made in the IAM-method [13], but without changing the results within its standard deviations. The limitations of the present analysis are also indicated by the rather small value of 3.091 amuÅ^2 for I_α (e.g. see [4]) and the magnitude of the angle $\sphericalangle(a, i)$ which can only be made consistent with the molecular structure under the assumption of an improbable C–C–CH$_3$-angle.

Finally, the results from the Stark effect analysis are given in Table 5. The fitted dipole moment components are in good agreement with the estimates $\mu_a = 3.2$ D and $\mu_b = 0.5$ D obtained from the dipole moment of isoxazole [13], using dipole increments of 0.63 D and 1.0 D for the $\rangle$CH and the $\rangle$CCH$_3$ group, respectively. The most probable alignment of the total dipole moment μ is shown in Figure 2.

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