# The Microwave Spectrum of 4-Methylisothiazole

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The microwave spectrum of 4-methylisothiazole was assigned by means of a pulsed molecular beam microwave Fourier transform spectrometer. Analysis of the spectrum yielded the rotational constants $A = 7370.642(31)$ MHz, $B = 2515.8461(30)$ MHz, $C = 1897.2863(33)$ MHz, a threefold barrier to internal rotation of the methyl group of $V_3 = 3170.81(130)$ GHz $\triangleq 105.7669(430)$ cm$^{-1}$, a momentum of inertia of the methyl group of $I_\alpha = 3.16769(130)$ amu $\cdot$ Å$^2$ and an angle between internal rotor axis and principal $a$-axis of $\Theta = 5.406(38)°$. The nitrogen quadrupole coupling constants were determined to be $\chi^+ = \chi_{bb} + \chi_{cc} = 1.4822(14)$ MHz, $\chi^- = \chi_{bb} - \chi_{cc} = -1.4353(25)$ MHz and $\chi_{ab} = -3.16(12)$ MHz.

## Introduction

4-Methylisothiazole is a molecule with both a methyl group as an internal rotor and nitrogen as a quadrupole nucleus. Since the barrier to internal rotation was assumed to be rather low [1] we expected a spectrum with widely separated A and E species transitions with the individual lines being split by nitrogen quadrupole coupling. In contrast to rigid molecules without internal rotation, in this case the complete quadrupole coupling tensor can be determined since the off-diagonal element of the $\chi$-tensor comes in via the non-zero expectation value $\langle J_a J_b + J_b J_a \rangle$. Only a few molecules of this type have been investigated so far [2]. First attempts to assign the spectra obtained from measurements with a Stark spectrometer and with a waveguide Fourier transform spectrometer failed because of the presence of higher vibrotorsionally excited states. So we decided to carry out all measurements with a pulsed molecular beam microwave Fourier transform (MB-MWFT) spectrometer [3].

## Experimental Details

The first step taken was to scan the whole K band region (18 to 26.4 GHz) with a Stark spectrometer. A densely crowded spectrum composed of weak lines was obtained. No assignment based on a rigid rotor model using estimated structural parameters of isothiazole [4] was possible. So we decided to scan a frequency range from 8.3–9.7 GHz using our automatic MB-MWFT spectrometer [3]. A sample containing 1–2% 4-methylisothiazole [5] in argon and a stagnation pressure of 30–60 kPa was used throughout. This scan was much clearer because of the absence of higher vibrotorsionally excited states. A number of strong lines were found and subsequently remeasured in the high resolution mode of the spectrometer [6], where a linewidth of approximately 2 kHz (FWHH) can be achieved. The nitrogen hyperfine structures were completely resolved.

## Spectral Analysis

### *Internal Rotation*

We started the spectral assignment with the search for $a$-type A-species transitions since they behave roughly like rigid rotor lines and their appearance in the spectrum could be predicted from our estimated rotational constants $A = 7364$ MHz, $b = 2523$ MHz, $C = 1902$ MHz derived from the assumed structural parameters given in Table 1 (see also Figure 1). The search was guided by the nitrogen hyperfine structure which was compared with the prediction obtained from estimated coupling constants. After assigning also the $b$-type A-species transitions we subsequently predicted E-species lines for various barrier to internal rotation $V_3$. The program we used for these calculations was VC3IAM [7]. Due to the lack of higher $J$ transitions no centrifugal distortion was fitted. The angle $\Theta$ between the internal rotor axis and the principal $a$-axis as well as the momentum of inertia $I_\alpha$ of the methyl group were estimated from standard struc-

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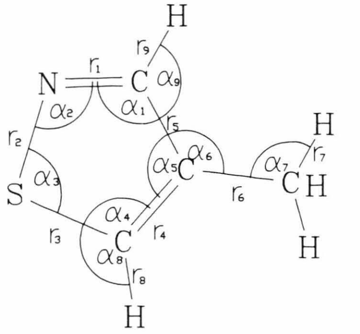

Fig. 1. Assumed structure of 4-methylisothiazole. Bond lengths and angles are given in Table 1.

Table 1. Assumed structural parameters of 4-methylisothiazol [4]. Bond distances and angles are defined in Figure 1.

| Distances/Å | Angles/° |
|---|---|
| $r_1 = 1.322$ | $a_1 = 116.67$ |
| $r_2 = 1.646$ | $a_2 = 108.88$ |
| $r_3 = 1.702$ | $a_3 = 95.69$ |
| $r_4 = 1.374$ | $a_4 = 108.77$ |
| $r_5 = 1.418$ | $a_5 = 110.00$ |
| $r_6 = 1.520$ | $a_6 = 125.21$ |
| $r_7 = 1.085$ | $a_7 = 110.00$ |
| $r_8 = 1.085$ | $a_8 = 121.73$ |
| $r_9 = 1.085$ | $a_9 = 121.70$ |

Table 2. Hyperfine free transition line centers for the A and E internal rotor states of 4-methylisothiazole.

| $J\,K_a\,K_c$ | $J'\,K'_a\,K'_c$ | $\nu_{\text{obs}}$(A) [GHz] | $\nu_{\text{obs-calc}}$(A) [kHz] | $\nu_{\text{obs}}$(E) [GHz] | $\nu_{\text{obs-calc}}$(E) [kHz] |
|---|---|---|---|---|---|
| 1 1 1 | 0 0 0 | 9.358309 | −33 | 7.703000 | −13 |
| 2 0 2 | 1 0 1 | 8.772024 | −36 | 8.767477 | 24 |
| 2 1 1 | 1 1 0 | 9.444971 | −33 | 9.024674 | 40 |
| 2 1 2 | 1 1 1 | 8.207991 | −28 | 8.628178 | 43 |
| 3 0 3 | 2 1 2 | 8.643590 | −38 | – | – |
| 4 0 4 | 3 1 2 | – | – | 9.143521 | 34 |
| 4 1 3 | 4 0 4 | 8.983124 | −3 | 9.382571 | 48 |
| 5 1 4 | 5 1 5 | 9.194059 | 9 | 9.890222 | −18 |

tural parameters. Finally all A- and E-species lines could be assigned. No extra lines were found within the covered frequency range. A fit of the hyperfine patterns (see below) yielded the corrected center frequencies given in Table 2. It should be noted that only for the A-species both the $K_a$ and $K_c$ pseudo quantum numbers are useful for the designation of energy levels.

Table 3. Rotation and internal rotation constants of 4-methylisothiazole with corresponding correlation matrix and overall freedom coefficients as defined in [8].

$A$/MHz = 7370.642(31)
$B$/MHz = 2515.8461(30)
$C$/MHz = 1897.2863(33)
$V_3$/GHz = 3170.81(130)
/cm$^{-1}$ = 105.7669(430)
/J · mol$^{-1}$ = 1265.252(510)
$I_\alpha$/amu · Å$^2$ = 3.16769(130)
$\Theta$/° = 5.406(38)

| | $A$ | $B$ | $C$ | $V_3$ | $I_\alpha$ | $\Theta$ | Freedom |
|---|---|---|---|---|---|---|---|
| $A$ | 1.000 | | | | | | 0.534 |
| $B$ | −0.137 | 1.000 | | | | | 0.555 |
| $C$ | −0.023 | 0.853 | 1.000 | | | | 0.449 |
| $V_3$ | 0.626 | −0.053 | −0.047 | 1.000 | | | 0.016 |
| $I_\alpha$ | −0.631 | 0.054 | 0.041 | −0.993 | 1.000 | | 0.017 |
| $\Theta$ | −0.680 | 0.065 | 0.150 | −0.593 | 0.590 | 1.000 | 0.218 |

In the case of E-species transitions only the $K_a$ quantum number is of some significance. All internal rotation parameters and the corresponding correlation matrix are compiled in Table 3. The reduced potential $S$ amounts to only 8.427377(61).

### *Nitrogen Quadrupole Hyperfine Structure*

The analysis of the nitrogen hyperfine patterns is based on the first order Hamiltonian [2]

$$H_{\text{NQ}} = (2/J(J+1))\,[\chi_{aa}\langle J_a^2\rangle + \chi_{bb}\langle J_b^2\rangle + \chi_{cc}\langle J_c^2\rangle + \chi_{ab}\langle J_a J_b + J_b J_a\rangle]\, f(I, J, F).$$

The brackets $\langle\ \rangle$ denote the expectation values of the various combinations of angular momentum components. $f(I, J, F)$ is the Casimir function. In rigid rotors the expectation value $\langle J_a J_b + J_b J_a\rangle$ vanishes and therefore no determination of $\chi_{ab}$ is possible within the first order approximation. If an internal rotor is present, however, the Coriolis term is usually nonzero and the determination of $\chi_{ab}$ becomes feasible. These calculations were carried out in a free-rotor basis.

Table 4 shows all hyperfine components used for the determination of the $\chi$-tensor. The expectation values of the angular momenta were calculated using the internal rotation data given in Table 3. Both the A- and E-species were fitted simultaneously, the results and the corresponding correlation matrix are shown in Table 5.

Table 4. Hyperfine components of transitions for the A and E internal rotor states of 4-methylisothiazole.

| $J\ K_a K_c$ | $J'\ K'_a K'_c$ | $F$ | $F'$ | $\nu_{obs}$(A) [GHz] | $\nu_{obs\text{-}calc}$(A) [kHz] | $\nu_{obs}$(E) [GHz] | $\nu_{obs\text{-}calc}$(E) [kHz] |
|---|---|---|---|---|---|---|---|
| 1 1 1 | 0 0 0 | | | | | | |
| | | 2 | 1 | 9.3583091 | 1.5 | 7.7029733 | 1.4 |
| | | 1 | 1 | 9.3583184 | 2.5 | 7.7031403 | −0.4 |
| | | 0 | 1 | 9.3582901 | −5.2 | 7.7027185 | −0.0 |
| 2 0 2 | 1 0 1 | | | | | | |
| | | 3 | 2 | 8.7720609 | −0.4 | 8.7675146 | 0.4 |
| | | 2 | 1 | 8.7720074 | 2.4 | 8.7674557 | −0.1 |
| | | 1 | 0 | 8.7716712 | −0.4 | 8.7671362 | 0.6 |
| | | 2 | 2 | 8.7715593 | 0.1 | 8.7670198 | −0.8 |
| | | 1 | 1 | 8.7727830 | −2.9 | 8.7682240 | 0.5 |
| 2 1 1 | 1 1 0 | | | | | | |
| | | 3 | 2 | 9.4450435 | −2.4 | 9.0247476 | −0.1 |
| | | 2 | 1 | 9.4446016 | 2.0 | 9.0243502 | 0.7 |
| | | 1 | 0 | 9.4457066 | −0.4 | 9.0252203 | −0.1 |
| | | 2 | 2 | – | – | 9.0246140 | −1.8 |
| | | 1 | 1 | – | – | 9.0245537 | −0.9 |
| 2 1 2 | 1 1 1 | | | | | | |
| | | 3 | 2 | 8.2080942 | −2.3 | 8.6282833 | −0.6 |
| | | 2 | 1 | 8.2076196 | 0.0 | 8.6277659 | 0.7 |
| | | 1 | 0 | 8.2083713 | 2.0 | 8.6287319 | 0.4 |
| | | 2 | 2 | – | – | 8.6279337 | −0.4 |
| | | 1 | 1 | 8.2083496 | 0.9 | 8.6283098 | 0.5 |
| 3 0 3 | 2 1 2 | | | | | | |
| | | 4 | 3 | 8.6436252 | 0.0 | – | – |
| | | 3 | 2 | 8.6435369 | 0.4 | – | – |
| | | 2 | 1 | 8.6435589 | −1.0 | – | – |
| 4 0 4 | 3 1 2 | | | | | | |
| | | 5 | 4 | – | – | 9.1436330 | 0.1 |
| | | 4 | 3 | – | – | 9.1432250 | −1.2 |
| | | 3 | 2 | – | – | 9.1437200 | 1.8 |
| 4 1 3 | 4 0 4 | | | | | | |
| | | 5 | 5 | 8.9830160 | 0.5 | 9.3824724 | 1.0 |
| | | 4 | 4 | 8.9834243 | 1.9 | 9.3828457 | 0.8 |
| | | 3 | 3 | 8.9829095 | −1.3 | 9.3823742 | −1.1 |
| 5 1 4 | 5 1 5 | | | | | | |
| | | 6 | 6 | 9.1939258 | 1.2 | 9.8900965 | 0.1 |
| | | 5 | 5 | 9.1944084 | 0.0 | 9.8905491 | 0.4 |
| | | 4 | 4 | 9.1938245 | −1.6 | 9.8900019 | −2.3 |

Table 5. Nitrogen quadrupole coupling constants of 4-methylisothiazole with corresponding correlation matrix and overall freedom coefficients as defined in [8].

$\chi^+$ /MHz = 1.4822(14)
$\chi^-$ /MHz = −1.4353(25)
$\chi_{ab}$/MHz = −3.16(12)

| | $\chi^+$ | $\chi^-$ | $\chi_{ab}$ | Freedom |
|---|---|---|---|---|
| $\chi^+$ | 1.000 | | | 0.972 |
| $\chi^-$ | −0.077 | 1.000 | | 0.995 |
| $\chi_{ab}$ | −0.316 | 0.032 | 1.000 | 0.975 |

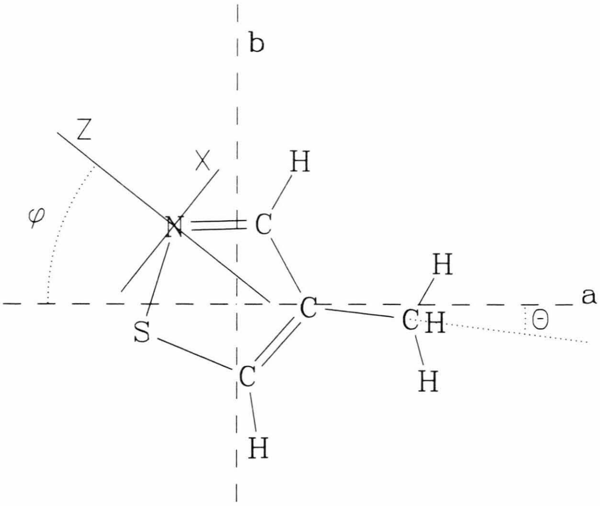

Fig. 2. 4-Methylisothiazole in its principal axis systems of the rotational inertia tensor ($a$, $b$) and the quadrupole coupling tensor ($x$, $z$).

## Discussion

The rotational constants of 4-methylisothiazole agree quite well with the prediction obtained from the structural assumptions given in Table 1. The barrier to internal rotation of 105.8 $\text{cm}^{-1}$ is roughly half as high as in the case of the corresponding 4-methylisoxazole with a barrier of 258.6 $\text{cm}^{-1}$ [9]. It should be noted that always a pure threefold potential without any sixfold and higher contributions was assumed. This assumption was made since no torsionally excited states with $|m| > 1$ were measured and thus no simultaneous determination of various potential coefficients was possible. We were able to determine the complete quadrupole coupling tensor of the nitrogen nucleus in the principal inertia axes system. This is due to the fact that the expectation value $\langle J_a J_b + J_b J_a \rangle$ does not vanish as it happens in the case of rigid molecules without internal rotation. Transformation of the quadrupole coupling tensor to its principal axes system, i.e. diagonalization of the tensor, is achieved by a rotation in the plane of symmetry by an angle of 38.3°. Both the principal inertia axes system and the principal axes system of the coupling tensor are shown in Figure 2. Obviously the $x$-axis of the coupling tensor at the nitrogen nucleus does not point along the bisector of the C–N–S angle. Further work on various thiazoles and isothiazoles is in progress.

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