Centrifugal Distortion and Internal Rotation Analysis of the Rotational Spectrum of Methyl Thiocyanate

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The ground state rotational spectrum of methyl thiocyanate has been investigated between 7 and 300 GHz ($J \leq 38$ and $K \leq 25$). An overall fit of the measurements using the Internal Axis Method has allowed us to accurately determine the internal rotation parameters. For the $A$ sub-state effective rotational parameters are given which allow the calculation of transition frequencies of possible astrophysical interest.

The microwave spectrum of methyl thiocyanate (CH$_3$SCN) was first successfully analyzed by Nakagawa et al. [1] who determined the rotational constants, the $\mu_a$ component of the dipole moment and the barrier. A little later Dreizler [2] was able to measure $\mu_b$ transitions and to determine the quadrupole coupling constants of $^{14}$N. He also established that the barrier to internal rotation was not the same in the first excited torsional state as in the ground state. He subsequently developed a molecular model with five degrees of freedom to simulate the internal rotation splittings in the ground state and in excited torsional and vibrational states [3]. Thanks to extensive measurements of isotopic species Dreizler and coll. [4] determined a complete $r_5$ structure, the $\mu_a$ and $\mu_b$ components of the dipole moment inclusive of relative sign, and the complete $^{14}$N quadrupole tensor. However, the available measurements were not sufficient to determine accurate centrifugal distortion constants. As methyl thiocyanate could be a possible candidate for interstellar detection, we have remeasured its ground state rotational spectrum and carried out a complete centrifugal distortion analysis so that accurate measurements and predictions would be available for the radioastronomers. We have also performed a new and more complete internal rotational analysis with the more accurate IAM (Internal Axis Method).

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Table 1. Measured ground state transitions of CH₃SCN.

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Table 1 (continued)
Table 2. Molecular parameters for methyl thiocyanate.

- Angle between the inertia axis \( a \) and the internal rotation axis \( i \).
- Moment of inertia of the methyl group.
- Standard deviation of the fit.

The correlation coefficients are given in Table 3.

### Rotational constants

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<td>( C ) [MHz]</td>
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### Centrifugal distortion constants

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<th>( \Delta_K ) [kHz]</th>
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### Internal rotation parameters

- \( V_3 \) [cal. mole\(^{-1}\)] = 1577.2 (59)
- \( \xi (i, a) \) [°] = 57.576 (119)
- \( I_s \) [u.Å²] = 3.2090 (140)

### Correlation coefficients

#### Rotational and centrifugal distortion constants (fit of the A lines)

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#### Internal rotation parameters

- \( V_3 \) = 1577(6) cal/mole
- \( \xi (i, a) \) = -0.481
- \( I_s \) = 0.976

Parameters but the standard deviation decreases to 0.082 MHz. Likewise, a conventional centrifugal distortion analysis of the A-lines gives a standard deviation of only 73 kHz. The higher standard deviation for the simultaneous fit of the A- and E-lines is due to the fact that the splittings of some doublets could not be resolved. To derive the effective parameters listed in the second column of Table 2 the Hamiltonian of Watson (Eq. (68) of [9]) was used. The results are given for the representation \( I' \) in the A reduction. They may be used for the prediction of frequencies with possible radioastronomical interest. In the internal rotation analysis the differences between the calculated and observed frequencies (Table 1) are greater than the experimental accuracy, especially for the high \( J \) transitions. This result seems quite general [10] and probably shows that the rigid frame-rigid top model with one torsional degree of freedom is failing for high \( J \) transitions.

Our value for the barrier to internal rotation: \( V_3 = 1577(6) \) cal/mole is in good agreement with the previous determination from the ground state splittings: \( V_3 = 1600(80) \) cal/mole [11], but it is much more precise. Andresen and Dreizler [12] obtained a value for \( V_3 \) from the simultaneous analysis of the splittings of the rotational transitions in four states: ground state, first excited torsional state and the lowest excited states of the CSC in plane bend. Their \( V_3 = 1618 \) cal/mole is, however,
not directly comparable to ours because they use further potential coefficients. 

$I_2$ may be determined quite independently using 

$$I_2 = I_a + I_b - I_e + \Delta.$$ 

If the effects of the vibrations are ignored ($\Delta = 0$), the effective moment of inertia $I_2^0 = 2.934 \text{ u.A}^2$ is obtained. A better method is to use the changes in moments of inertia for the normal and deuterated species:

$$I_2 = (I_a + I_b - I_e)_{\text{CD}_3\text{SCN}} - (I_a + I_b - I_e)_{\text{CH}_3\text{SCN}} + \Delta (\text{CD}_3) - \Delta (\text{CH}_3).$$

If it is assumed that $\Delta (\text{CD}_3) = \Delta (\text{CH}_3)$, the substitution moment of inertia is obtained: $I_2^0 = 3.289 \text{ u.A}^2$. Laurie [13] has shown that this approximation is in general good. $I_2^0$ is much too low. This is not surprising because for CH$_3$SCN the CSC in-plane bending is very low: $v_{10} = 170 \text{ cm}^{-1}$ [14]. Herschbach and Laurie [15] have proposed an approximation which attributes the major part of the inertial defect to the lowest in-plane vibration: 

$$\Delta = 4 K_{10} = 0.394 \text{ u.A}^2.$$ 

This correction is indeed of the correct order of magnitude. On the other hand $I_2^0$ is too high, contrary to what was always observed up to now [8]. It could be simply explained by the fact that the inertial defect $\Delta$ is smaller for the heavier isotopic species.

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