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 ($J \leqq 38$ and $K_- \leqq 25$). An overall fit of the measurements using the Internal Axis Method has allowed us to accurately determine the internal rotation parameters. For the A substate effective rotational parameters are given which allow the calculation of transition frequencies of possible astrophysical interest.

The microwave spectrum of methyl thiocyanate (CH_3SCN) was first successfully analyzed by Nakagawa et al. [1] who determined the rotational constants, the μ_a component of the dipole moment and the barrier.

A little later Dreizler [2] was able to measure μ_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 simultaneous analyze 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_s structure, the μ_a and μ_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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The centimeterwave frequencies were taken from Dreizler and Mirri [3]. A few additional measurements were made with the Utrecht microwave-microwave double resonance spectrometer. The other measurements were performed with the Lille millimeterwave spectrometer [5]. The data are collected in Table 1.

The molecular parameters were derived from the observed frequencies by means of an IAM-based least-squares computer program. This program is similar to the one reported earlier [6], but it is written in FORTRAN and it allows refinement of the quartic and sextic centrifugal distortion constants. The centrifugal distortion terms were defined in the Principal Axis System (representation I^r), transformed to the Internal Axis System, and added to the Hamiltonian. Basis functions $\exp i\,\alpha(3k+\sigma)$, with k ranging from -10 to $+10$, were used, and in the Van Vleck transformation the summation over excited torsional states was carried out up to $v=4$. In all calculations A- and E-type lines were given equal weights. The determined parameters are given in the first column of Table 2. As usual [7], the correlation is the greatest between V_3 and I_α: -0.976, nevertheless, I_α is well enough determined and its value: $I_\alpha = 3.209$ u.Å^2 is of the expected order of magnitude, as may be seen from inspection of Table V of [8]. The standard deviation is 0.158 MHz for the A-lines and 0.177 MHz for the E-lines. If the sextic terms are not included into the fit the standard deviation rises to 1.135 MHz for the A-lines and 1.148 MHz for the E-lines. A direct determination of the internal rotation parameters V_3, I_α, and $\measuredangle(i, a)$ from the splittings (instead of the frequencies) gives the same values for these

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Table 1. Measured ground state transitions of CH_3SCN.

J'	K'_-	K'_+	←	J	K_-	K_+	ν_A[MHz]	calc-exp	ν_E[MHz]	calc-exp
2	1	2		1	0	1	25849.372	-0.133	25849.372	-0.565
2	1	2		1	1	1	14217.985	-0.090	14217.985	-0.144
3	0	3		2	1	2	11499.664	-0.052	11499.664	0.054
3	1	2		3	0	3	14610.415	-0.111	14609.800	-0.120
4	1	3		3	1	2	31557.506	-0.225	31557.141	-0.274
4	1	3		4	0	4	16523.604	-0.133	16522.758	-0.098
4	1	3		4	1	4	8005.738	-0.021	8005.025	-0.017
5	1	4		5	0	5	19110.070	-0.107	19108.993	-0.099
5	1	4		5	1	5	11986.421	-0.042	11985.336	-0.019
6	1	5		5	1	4	47104.880	-0.036	47104.321	-0.368
6	2	4		5	2	3	46177.213	0.327	46177.213	-0.265
6	1	5		6	0	6	22460.196	-0.408	22458.794	-0.414
6	1	5		6	1	6	16724.990	-0.068	16723.499	-0.053
7	1	6		7	0	7	26631.716	-0.152	26629.878	-0.138
7	1	6		7	1	7	22179.519	-0.167	22177.547	-0.137
7	2	5		7	1	6	30160.864	-0.485	30159.980	-0.460
8	1	7		8	1	8	28285.323	-0.090	28282.839	-0.058
8	2	6		8	1	7	30171.992	-0.305	30170.985	-0.291
8	2	6		8	2	7	7374.715	0.007	7373.757	0.014
9	2	7		9	2	8	10948.386	-0.031	10946.924	0.054
10	2	8		10	2	9	15370.386	-0.003	15368.502	0.010
11	2	9		10	3	8	37057.760	0.131	37057.760	-0.351
11	2	9		11	1	10	34763.850	-0.223	34761.950	-0.261
11	2	9		11	2	10	20621.581	-0.016	20619.119	0.025
12	2	10		11	2	9	94419.430	-0.563	94418.140	-0.449
12	2	10		12	1	11	38109.530	-0.220	38107.050	-0.185
12	2	10		12	2	11	26655.556	0.018	26652.443	0.115
13	3	11		12	3	10	98111.540	-0.466	98110.610	-0.401
13	4	9		12	4	8	98871.800	-0.584	98870.330	-0.403
13	2	11		13	2	12	33403.375	0.108	33399.735	0.110
13	3	10		13	3	11	8177.770	-0.001	8176.381	0.021
14	3	11		14	3	12	11813.367	0.058	11811.402	0.110
16	3	14		15	4	11	31794.370	-0.130	31796.640	-0.138
17	3	14		17	3	15	28191.089	0.153	28187.073	0.218
22	2	20		21	4	17	35338.090	0.066	35344.510	-0.011
28	4	24		27	4	23	219754.925	0.014	219753.179	0.000
28	5	23		27	5	22	220213.846	0.030	220211.226	0.058
29	3	26		28	3	25	218432.177	-0.018	218431.299	-0.009
29	5	25		28	5	24	220337.429	0.075	220335.856	0.079
29	7	23		28	7	22	221162.225	0.120	221160.694	0.115
29	8	22		28	8	21	220414.586	0.076	220415.791	0.109
29	8	21		28	8	20	220447.390	0.082	220443.332	-0.065

Table 1 (continued)

J'	K'_-	K'_+	←	J	K_-	K_+	ν_A[MHz]	calc-exp	ν_E[MHz]	calc-exp
29	10	19		28	10	18	219455.276	0.083	219453.325	-0.003
29	10	20		28	10	19	219455.276	-0.005	219455.276	0.001
29	11	18		28	11	17	219172.599	-0.111	219170.731	-0.059
29	11	19		28	11	18	219172.599	-0.114	219172.599	0.119
29	12	17		28	12	16	218963.698	0.005	218962.140	-0.061
29	12	18		28	12	17	218963.698	0.005	218964.181	0.014
29	13	17		28	13	16	218806.071	0.030	218806.870	-0.026
29	14	15		28	14	14	218685.253	0.004	218684.105	-0.055
29	14	16		28	14	15	218685.253	0.004	218686.282	-0.042
29	15	14		28	15	13	218591.660	-0.023	218590.680	-0.022
29	15	15		28	15	14	218591.660	-0.023	218592.858	-0.010
29	16	13		28	16	12	218518.695	0.006	218517.971	-0.010
29	16	14		28	16	13	218518.695	0.006	218520.096	0.029
29	19	10		28	19	9	218383.803	-0.068	218383.803	-0.036
29	19	11		28	19	10	218383.803	-0.068	218385.632	0.060
29	20	9		28	20	8	218358.243	-0.081	218358.243	0.219
29	20	10		28	20	9	218358.243	-0.081	218360.170	0.084
29	21	8		28	21	7	218339.578	-0.069	218340.056	0.022
29	21	9		28	21	8	218339.578	-0.069	218341.595	0.117
30	2	28		29	2	27	217198.268	0.022	217197.555	-0.017
30	3	28		29	3	27	217017.286	0.081	217016.523	0.047
38	12	26		37	12	25	287788.810	-0.146	287786.685	-0.067
38	13	25		37	13	24	287414.261	-0.015	287412.491	-0.026
38	14	25		37	14	24	287126.217	-0.011	287127.196	-0.029
38	14	24		37	14	23	287126.217	-0.011	287124.729	-0.051
38	15	24		37	15	23	286900.815	-0.016	286902.051	-0.019
38	15	23		37	15	22	286900.815	-0.016	286899.526	0.010
38	16	23		37	16	22	286722.279	-0.040	286723.752	-0.026
38	16	22		37	16	21	286722.279	-0.040	286721.310	-0.058
38	17	22		37	17	21	286579.613	-0.014	286581.323	-0.002
38	18	21		37	18	20	286464.929	0.149	286466.928	0.084
38	19	20		37	19	19	286372.936	0.024	286374.990	0.092
38	20	19		37	20	18	286299.063	-0.095	286301.172	0.081
38	21	18		37	21	17	286239.922	-0.079	286242.108	0.155
38	22	17		37	22	16	286193.111	-0.052	286195.517	0.067
38	23	16		37	23	15	286156.698	-0.068	286159.100	0.129
38	23	15		37	23	14	286156.698	-0.068	286157.728	0.012
38	24	15		37	24	14	286129.137	-0.162	286131.527	0.087
38	24	14		37	24	13	286129.137	-0.162	286130.361	0.014
38	25	14		37	25	13	286108.942	-0.125	286111.382	0.081
38	25	13		37	25	12	286108.942	-0.125	286110.381	0.116

Table 2. Molecular parameters for methyl thiocyanate. $\measuredangle(i, a)$: Angle between the inertia axis a and the internal rotation axis i. I_α: Moment of inertia of the methyl group. σ: Standard deviation of the fit. Standard errors in units of the last digit in brackets. The correlation coefficients are given in Table 3.

	Direct fit of the experimental frequencies	Fit of the A lines
Rotational constants		
A [MHz]	15 787.0292(184)	15 787.2553 (145)
B [MHz]	4 155.67034(183)	4 155.65561(158)
C [MHz]	3 353.7661 (54)	3 354.09664(150)
Centrifugal distortion constants		
Δ_J [kHz]	2.3197 (27)	2.33070(156)
Δ_{JK} [kHz]	− 10.8103 (136)	− 9.3517 (136)
Δ_K [kHz]	157.08 (110)	159.73 (79)
δ_J [kHz]	0.76253 (87)	0.77758(210)
δ_K [kHz]	13.102 (102)	11.533 (102)
Φ_{JK} [Hz]	0.0594 (43)	0 [a]
Φ_{KJ} [Hz]	− 0.8791 (128)	− 0.4874 (64)
φ_J [Hz]	0 [a]	0.00928(134)
φ_{JK} [Hz]	0.222 (55)	0 [a]
φ_K [Hz]	0 [a]	− 2.076 (53)
σ [MHz]	0.160	0.073
Internal rotation parameters [c]		
V_3 [cal. mole^{-1}] [b]	1 577.2 (59)	
$\measuredangle(i, a)$ [°]	57.576 (119)	
I_α [u.Å^2]	3.2090 (140)	

[a] Fixed value.
[b] 1 cal·mole^{-1} = 10 492.4 MHz = 4.184 J·mole^{-1}.
[c] The internal rotation parameters were directly determined from the splittings.

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^r 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 lines. 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,

Table 3. Correlation coefficients.

Rotational and centrifugal distortion constants (fit of the A lines)											
A	1.000										
B	0.120	1.000									
C	0.031	0.836	1.000								
Δ_J	0.008	− 0.069	− 0.180	1.000							
Δ_{JK}	0.052	0.613	0.702	− 0.776	1.000						
Δ_K	0.811	− 0.262	− 0.282	− 0.065	− 0.116	1.000					
δ_J	− 0.095	0.658	0.523	− 0.687	0.827	− 0.304	1.000				
δ_K	0.076	− 0.539	− 0.621	0.846	− 0.944	0.206	− 0.903	1.000			
Φ_{KJ}	0.071	0.585	0.622	− 0.257	0.698	− 0.164	0.422	− 0.461	1.000		
φ_J	− 0.083	0.668	0.507	− 0.573	0.745	− 0.314	0.967	− 0.816	0.416	1.000	
φ_K	− 0.091	− 0.634	− 0.658	− 0.375	− 0.205	0.182	− 0.064	0.067	− 0.367	− 0.054	1.000
Internal rotation parameters											
V_3	1.000										
$\measuredangle(i, a)$	− 0.481	1.000									
I_α	− 0.976	0.482	1.000								

not directly comparable to ours because they use further potential coefficients.

I_α may be determined quite independently using

$$I_\alpha = I_a + I_b - I_c + \Delta .$$

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

$$I_\alpha = (I_a + I_b - I_c)_{CD_3SCN} - (I_a + I_b - I_c)_{CH_3SCN} + \Delta(CD_3) - \Delta(CH_3) .$$

If it is assumed that $\Delta(CD_3) = \Delta(CH_3)$, the substitution moment of inertia is obtained: $I_\alpha^s = 3.289$ u.Å^2. Laurie [13] has shown that this approximation is in general good. I_α^0 is much too low. This is not surprising because for CH_3SCN the CSC in-plane bending is very low: $\nu_{10} = 170\ cm^{-1}$ [14]. Herschbach and Laurie [15] have proposed an approximation which attributes the major part of the inertial defect to the lowest in-plane vibration: $\Delta = 4\,K/\omega = 0.394$ u.Å^2. This correction is indeed of the correct order of magnitude. On the other hand I_α^s 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 Δ is smaller for the heavier isotopic species.

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