Investigation of the ^{14}N Quadrupole Hyperfine Structure and the Stark Effect of Methyl Isocyanate and Methyl Isothiocyanate by Microwave Fourier Transform Spectroscopy

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The nitrogen ^{14}N quadrupole hyperfine structure and the Stark effect in the rotational spectra of methyl isocyanate and methyl isothiocyanate were investigated by high resolution microwave Fourier transform spectroscopy.

The components of the coupling tensor in the principal inertia axis system and the μ_a components of the dipole moments have been determined.

We investigated the nitrogen-hyperfine structure (hfs) and Stark effect in the rotational spectra of methyl isocyanate, CH_3NCO, and methyl isothiocyanate, CH_3NCS, by microwave Fourier transform (MWFT) spectroscopy. The rotational spectrum of methyl isocyanate was first measured and analyzed by Curl et al. [1] and Lett and Flygare [2]. More recently Koput [3] improved the analysis by the model of the quasisymmetric top. Methyl isothiocyanate was investigated by Beard and Dailey [4], Siegel [5] and again Lett and Flygare [2]. Also this molecule is an example for a quasi-symmetric top and is presently under investigation by Koput [6].

As in both molecules the barriers to internal rotation are small, CH_3NCO: $V_3 = 83(15)$ cal/mol [2] and $V_3^{\text{eff}} = 59.20(29)$ cal/mol [6] for a linear NCO chain, $V_3^{\text{eff}} = 58.92(31)$ cal/mol [6] for a bent NCO chain and CH_3NCS: $V_3 = 304(50)$ cal/mol [2], we concentrated on the internal rotation ground state $m = 0$ and on the vibrational ground state to have a minimum influence of the low frequency CNC-bending vibration. The values of V_3 and V_3^{eff} differ by the model assumptions.

The measurements by MWFT spectroscopy [7–9] are given in Tables 1 a and 1 b. Figures 1 and 2 give two examples of the recordings. The temperatures were around -25 °C, the pressures 0.3 mTorr. The experimental data are sufficient to determine the ^{14}N-hfs completely. For the analysis we assumed, that the rotational spectrum in the $m = 0$ state is in approximation a rigid asymmetric rotor spectrum. The results are given in Tables 2 a and 2 b. The rotational constants were taken from [2]. For methyl isothiocyanate a reassignment [6] of the spectrum was helpful. The hfs coupling constants χ_+ and χ_- were evaluated by first order theory. There is no

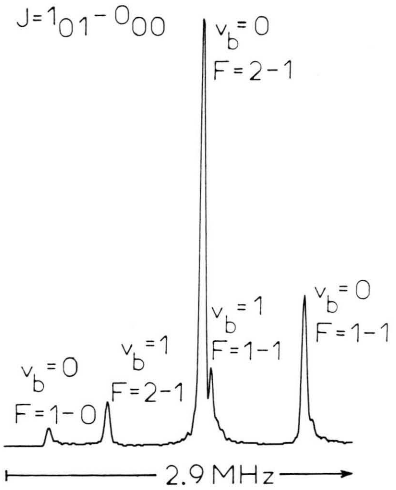

Fig. 1. $J = 1_{01} - 0_{00}$ transition of methyl isocyanate. A section of 2.9 MHz out of a 25 MHz range of the power spectrum is given. Sample interval 20 ns, 1920 k cycles, 1024 data points supplemented by 3072 zeros, pressure 0.3 mTorr, temperature -25 °C.

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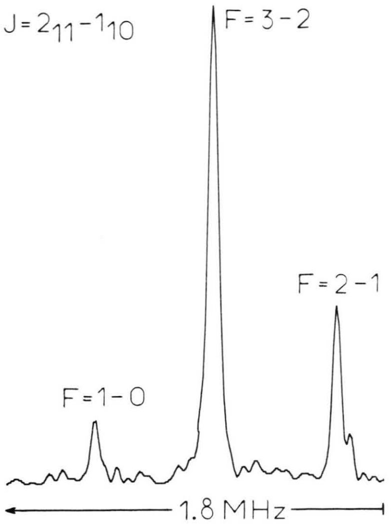

Fig. 2. $J = 2_{11} - 1_{10}$ transition of methyl isothiocyanate. A section of 1.8 MHz out of a 25 MHz range of the power spectrum is given. Sample interval 20 ns, 640 k cycles, 1024 data points, supplemented by 3072 zeros, pressure 0.4 mTorr, temperature – 22 °C.

Table 1 a. Measured frequencies ν_{obs} of methyl isocyanate refined by a contour analysis of overlying hfs components. ν_{unsplit} is obtained adding the hfs-correction to the frequencies ν_{obs} of the hfs components. $\Delta\nu_{\text{obs}}$ and $\Delta\nu_{\text{calc}}$ experimental and calculated hfs splittings. Frequencies in MHz.

$J'\ K'_-\ K'_+ - J$	$K_-\ K_+$	$F'F$	ν_{obs}	ν_{unsplit}	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{calc}}$
1 0 1–0	0 0	1–1	8 672.079	8 671.369		
		2–1	8 671.224		0.855	0.851
		0–1	8 669.954		1.270	1.276
2 0 2–1	0 1	2–2	17 343.379	17 342.529		
		1–0	17 343.234		0.145	0.142
		2–1	17 342.536		0.698	0.709
		3–2	17 342.467		0.069	0.061
2 1 1–1	1 0	2–1	17 505.322	17 504.688		
		3–2	17 504.439		0.883	0.878
		1–0	17 503.509		0.930	0.927
2 1 2–1	1 1	2–1	17 191.082	17 190.371		
		3–2	17 190.197		0.885	0.884
		1–0	17 189.338		0.859	0.856

Table 1 b. Measured frequencies of methyl isothiocyanate. See Table 1 a.

$J'\ K'_-\ K'_+ - J$	$K_-\ K_+$	$F'F$	ν_{obs}	ν_{unsplit}	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{calc}}$
1 0 1–0	0 0	1–1	5 026.582	5 026.117		
		2–1	5 026.025		0.557	0.560
2 0 2–1	0 1	2–2	10 052.766	10 052.204		
		1–0	10 052.668		0.098	0.093
		2–1	10 052.209		0.459	0.467
		3–2	10 052.166		0.043	0.040
		1–1	10 051.262		0.904	0.893
2 1 1–1	1 0	2–1	10 107.051	10 106.586		
		3–2	10 106.469		0.582	0.584
		1–0	10 105.933		0.536	0.538
2 1 2–1	1 1	2–1	10 037.062	10 036.598		
		3–2	10 036.489		0.573	0.576
		1–0	10 035.856		0.633	0.635

Table 2 a. Rotational and quadrupole coupling constants of methyl isocyanate Standard deviation in brackets in units of the last digit. σ: Standard deviation of the fit, $\overline{\Delta\nu}$: mean experimental hfs-splitting.

A = 73 849.2 MHz from [2]
B = 4 392.22 MHz from [2]
C = 4 256.66 MHz from [2]
$\chi_+ = \chi_{bb} + \chi_{cc} = -\,2.8358(75)$ MHz
$\chi_- = \chi_{bb} - \chi_{cc} = 0.260(34)$ MHz
$\chi_{aa} = 2.8358(75)$ MHz
$\chi_{bb} = -\,1.288(21)$ MHz
$\chi_{cc} = -\,1.548(21)$ MHz
σ = 6 kHz
$\Delta\nu$ = 733 kHz
Correlation coefficient: $|\chi_+, \chi_-| = 0.001$

Table 2 b. Rotational and quadrupole coupling constants of methyl isothiocyanate. See Table 2 a.

A = 81 070.0 MHz from [2]
B = 2 537.01 MHz from [2]
C = 2 498.69 MHz from [2]
$\chi_+ = \chi_{bb} + \chi_{cc} = -\,1.8662(66)$ MHz
$\chi_- = \chi_{bb} - \chi_{cc} = -\,0.358(30)$ MHz
$\chi_{aa} = 1.8662(66)$ MHz
$\chi_{bb} = -\,1.112(18)$ MHz
$\chi_{cc} = -\,0.754(18)$ MHz
σ = 6 kHz
$\overline{\Delta\nu}$ = 487 kHz
Correlation coefficient: $|\chi_+, \chi_-| = 0.000$

transition in the range of our spectrometer which is sensitive to χ_{ab}.

As no isotopic species of the molecule with a sufficient rotation of principal inertia axes is available we could not calculate the principal axes components of the coupling tensor. It was further not feasible to estimate the principal axes of the coupling tensor, as none of its axes is correlated to a bond.

For comparison we give in Tables 3 a and 3 b quadrupole coupling constants of related molecules.

The measurements of the Stark effect were made in the region from 8 to 12.4 GHz. We constructed a cell with X-band waveguide with 22.86 × 10.16 mm

Table 3a. Quadrupole coupling constants [MHz] of some isocyanates.

Molecule	χ_{aa}	χ_{bb}	χ_{cc}	Ref.
H–NCO	2.056(11)	−0.473(10)	−1.583(10)	[12]
CH_3–NCO	2.8358(75)	−1.288(21)	−1.548(21)	this work
CH_3CH_2–NCO	2.529(16)	−1.137(20)	−1.392(20)	[13]

Table 3b. Quadrupole coupling constants [MHz] of some isothiocyanates.

Molecule	χ_{aa}	χ_{bb}	χ_{cc}	Ref.
H–NCS	1.114(26)	−0.530(71)	−0.585(71)	[14]
CH_3–NCS	1.8662(66)	−1.112(18)	−0.754(18)	this work
CH_3CH_2–NCS	1.873(18)	−1.264(26)	−0.609(26)	[15]

Table 4a. Measurement of the dipole moment μ_a of CH_3NCO for $J = 1_{01} - 0_{00}$, field free frequencies ν_{i0}: $\nu_{10} = 8669.954$ MHz, $\nu_{20} = 8671.224$ MHz, $\nu_{30} = 8672.079$ MHz;
ν_1: $F = 0 - 1$, $K = 0$, $M_F = 0$,
ν_2: $F = 2 - 1$, $K = 0$, $M_F = 0$,
ν_3: $F = 1 - 1$, $K = 0$, $|M_F| = 1$.
E [V/cm] field strength. See also Table 2a. Conversion factor: 1 D = $3.3356 \cdot 10^{-30}$ A s m.

E	ν_2	ν_3
19.441	8671.271	8672.104
38.826	8671.382	8672.216
58.260	8671.630	8672.409
77.553	8671.909	8672.674
96.988	8672.304	8673.056
116.374	8672.792	8673.552

$\mu_a = 2.882(8)$ D $= 9.613(27) \cdot 10^{-30}$ A s m
[1]: $\mu_a = 2.81(6)$ D $= 9.37(20) \cdot 10^{-30}$ A s m

Table 4b. Measurement of the dipole moment μ_a of CH_3NCS for $J = 2_{02} - 1_{01}$, field free frequency: $\nu_{10} = 10\,052.209$ MHz; ν_1: $F = 2 - 1$, $K = 0$, $|M_F| = 1$. See also Table 4a.

E	ν_1
38.825	10 052.147
77.549	10 051.752
116.374	10 051.053
155.159	10 050.059
194.004	10 048.766
232.743	10 047.244

$\mu_a = 3.453(3)$ D
$= 11.518(10) \cdot 10^{-30}$ A s m
[5]: $\mu_a = 3.41(3)$ D
$= 11.37(10) \cdot 10^{-30}$ A s m

$M_F = 0$

F	J \ F'	0	1			2			3		
	J'	1	0	1	2	1	2	3	2	3	4
0	1	$\xcancel{O}$	S		S						
1	0	S	$\xcancel{O}$	S	X	S					
	1		S	$\xcancel{O}$	S		S				
	2	S	X	S	$\xcancel{O}$	S		S			
2	1		S		S	$\xcancel{O}$	S	X	S		
	2			S		S	$\xcancel{O}$	S		S	
	3				S	X	S	$\xcancel{O}$	S		S
3	2					S		S	$\xcancel{O}$	S	X
	3						S		S	$\xcancel{O}$	S
	4							S	X	S	$\xcancel{O}$

Fig. 3. The $M_F = 0$ submatrix for $J = 1 - 0$ for molecules with one quadrupole nucleus with $I = 1$ (without K quantum numbers). The matrix elements come from: O: rotation; X: quadrupole coupling; S: Stark effect.

inner dimension and 3 m length. To have a sufficiently homogeneous Stark field we inserted a septum about 5 mm thick tapered on both ends and ending 5 mm before the waveguide windows. By this reflections at the septum ends are quickly damped with the aid of neighbouring waveguide isolators (compare Fig. 1 of [9], cell 21 replaced by the Stark cell). We estimated by the erroneous splitting of the $M = 0$ Stark lobe of the $J = 1 - 0$ line of Carbonylsulfide, OCS, that the precision of the position of the septum is better than 0.02 mm. OCS with $\mu = 0.71512(3)$ D [10] was used for calibration.

The measurements are given in Tables 4a and 4b. The Stark splittings were evaluated with the inclusion of ^{14}N quadrupole coupling. It was necessary to diagonalize the Hamiltonian matrix for the $M_F \geqq 1$ with the inclusion of elements from $F_{min} = M_F - 1$ to $F_{max} = J + I + 1$ for a given J (program EQ.FOR).

For $M_F = 0$ the matrix is given in Fig. 3 in the coupled symmetric top basis $|F M_F J K I\rangle$ [11]. For the fitting procedure the values for the rotational constants A, B, C and for the quadrupole coupling constants χ_+ and χ_- were taken from the Tables 2a and 2b.

Unfortunately only μ_a could be determined. The values are given in Table 4. No low J lines sensitive to μ_b are within the X-band.

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