Quadrupole Coupling in the Microwave Spectrum of Ethylisothiocyanate

An Application of Microwave Fourier Transform Spectroscopy

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We investigated the microwave spectrum of ethylisothiocyanate, CH_3CH_2 NCS, for the nitrogen quadrupole coupling. The spectrum was first measured and assigned by Sakaizumi, Ohashi, and Yamaguchi [1]. By comparing the measured rotational constants with those resulting from an assumed structure they concluded that the synperiplanar (cis) form was measured.

By use of Microwave Fourier Transform (MWFT) spectroscopy [2, 3] we were able to resolve the nitrogen quadrupole hfs. The sample was purchased from Ega Chemie, Steinheim, with a 95% purity and used after vacuum distillation. The spectra were recorded at temperatures of $-60\,^{\circ}C$ and pressures down to 0.2 mTorr.

The half width at half height was usually 30 kHz. We believe that our measurements are more precise than those reported. Our measuring error is less than 20 kHz*.

Figure 1 gives an example. The measured lines are given in Table 1. The hyperfine structure was analyzed by first order perturbation theory. This approximation was checked by calculations using diagonalisation of a sufficiently large Hamiltonian submatrix [4].

We further proved that no line within the range of our spectrometer is sensitive enough to the off diagonalelement χ_{ab} of the quadrupole coupling tensor. The results for the hfs-analysis are given in Table 2. The standard deviation of the fit is 8 kHz for a mean splitting of 230 kHz.

In the course of our analysis we performed a centrifugal distortion analysis to fourth order with the Hamiltonian of van Eijck [5] and Typke [6].

As the selection of lines with mostly $\Delta J = 1$, $\Delta K_- = 0$, $\Delta K_+ = 1$ is very unfavourable, nine correlation coefficients are higher than 0.99. So we set as in [1] $D_K' = 0$, $\delta_J' = 0$ and $R_6' = 0$. The results are given in Table 3. We included the lines of Table 1 and those lines of Table 1 of [1]** not measured by us.

* We monitor our high stability reference quartz by comparison with the normal frequency of DCF 77 Mainflingen.

** Lines of Table 1 of [1] marked with c) were exempted.

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The standard deviation of the fit of 52 lines measured by [1] and 17 lines measured by us are 210 kHz.

Using the full fourth order Hamiltonian [6] the standard deviation decreases to 192 kHz taking all lines. When we take $v = (\sum (\nu_{obs} - \nu_{calc})^2/n)^{1/2}$ as a measure of precision, we get 37 kHz for the 17 lines measured by MWFT-spectroscopy and 204 kHz for those of Table 1 of [1]. But as the correlation is high, we think that the set of constants of Table 3 is a good basis for further work.

We further repeated the calculations of the rotational constants by fitting the same structural parameters with the assumptions of Table 3 of [1] by a r_0-structure. The results are in agreement with [1].

Only few determinations of the hfs in isothiocyanates have been reported. The coupling constants are given in Table 4. The information for these molecules is too limited to determine the principal axes components of the coupling tensor.

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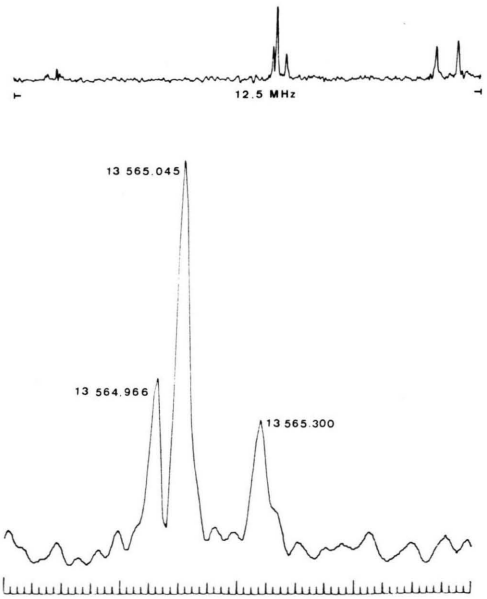

Fig. 1. Section of 1.5 MHz below a 12.5 MHz recording near the $4_{23} - 3_{22}$ transition of CH_3CH_2NCS. Temperature $-60\,^{\circ}C$, pressure 0.4 mTorr. Data aquisition: 1024 data points filled with zeros up to 4096 data points, 20 ns sample interval, time domain averaging 2^{18} cycles, frequency domain averaging 30 cycles, spectral point distance 12.5 kHz, line frequencies by three point interpolation.

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Table 1. Measured rotational transitions of ethylisothiocyanate. $\nu_{unsplit}$ is obtained adding the hfs-corrections to the frequencies ν_{obs} of the hfs components. Transitions below the line could not be resolved.

$J'_{K'_-K'_+} - J_{K_-K_+}$	$F' - F$	ν_{obs}	$\nu_{unsplit}$	$\Delta\nu_{hfs,obs}$	$\Delta\nu_{hfs,calc}$
$3_{21} - 2_{20}$	3 – 2	10 182.119			
	4 – 3	10 181.518	10 181.652	0.601	0.604
				0.334	0.335
	2 – 1	10 181.184			
$3_{03} - 2_{02}$	2 – 1	10 167.423	10 167.326	0.117	0.110
	4 – 3	10 167.306			
	3 – 2				
$3_{13} - 2_{12}$	3 – 2	9 922.446	9 922.315	0.187	0.166
	4 – 3	9 922.259			
	2 – 1				
$3_{22} - 2_{21}$	3 – 2	10 175.409			
	4 – 3	10 174.810	10 174.944	0.599	0.602
				0.332	0.334
	2 – 1	10 174.478			
$4_{04} - 3_{03}$	3 – 2	13 548.489	13 548.439	0.068	0.051
	5 – 4	13 548.421			
	4 – 3				
$4_{31} - 3_{30}$	4 – 3	13 571.676			
$4_{32} - 3_{31}$	5 – 4	13 571.127	13 571.253	0.549	0.558
				0.235	0.216
	3 – 2	13 570.892			
$4_{13} - 3_{12}$	4 – 3	13 896.687	13 896.634	0.091	0.076
	5 – 4	13 896.596			
$4_{14} - 3_{13}$	4 – 3	13 227.735	13 227.682	0.084	0.071
	5 – 4	13 227.651			
$4_{23} - 3_{22}$	4 – 3	13 565.298	13 565.110	0.256	0.255
	5 – 4	13 565.042			
	3 – 2	13 564.962		0.080	0.066
	3 – 2	13 564.962			
$5_{41} - 4_{40}$	5 – 4	16 966.290		0.487	0.505
$5_{42} - 4_{41}$	6 – 5	16 965.803	16 965.921	0.170	0.151
	4 – 3	16 965.633			
$5_{23} - 4_{22}$	5 – 4	16 987.627	16 987.520	0.164	0.142
	6 – 5	16 987.463			
	4 – 3				
$5_{05} - 4_{04}$	4 – 3	16 922.743	16 922.716	0.037	0.031
	6 – 5	16 922.706			
	5 – 4				
$5_{14} - 4_{13}$	5 – 4	17 367.246		0.023	0.015
	4 – 3	17 367.223	17 367.218	0.028	0.027
	6 – 5	17 367.195			
$5_{24} - 4_{23}$	5 – 4	16 954.108	16 954.015	0.138	0.138
	6 – 5	16 953.970			
	4 – 3				
$10_{19} - 10_{110}$	10 – 10	9 175.183	9 175.020	0.243	0.243
	11 – 11	9 174.940			
	9 – 9				
$2_{02} - 1_{01}$	3 – 2	6 781.050	6 781.050	0.000	0.040
	2 – 1				
$5_{15} - 4_{14}$	5 – 4				
	4 – 3	16 531.295	16 531.295	0.000	0.015
	6 – 5				0.029

Table 2. Nitrogen quadrupole coupling constants of ethylisothiocyanate (MHz). The errors are standard errors.

$\chi_+ = \chi_{bb} + \chi_{cc}$	−1.873 (18)	χ_{aa}	1.873 (18)
$\chi_- = \chi_{bb} - \chi_{cc}$	−0.656 (35)	χ_{bb}	−1.264 (26)
correlation coefficient	0.008	χ_{cc}	−0.609 (26)

Table 3. Rotational [MHz] and centrifugal [kHz] distortion constants of ethyisothiocyanate. Errors are standard errors. Assumption in square brackets. $\varkappa$: asymmetry parameter. $|(C, D'_J)|$: highest correlation.

A	14 188.5 (5.4)	D'_K	[0]
B	1 779.274 (6)	δ'_J	[0]
C	1 612.130 (6)	R'_6	[0]
D'_J	1.53 (4)	$\varkappa$	−0.973419
D'_{JK}	−36.84 (9)	$\lvert(C, D'_J)\rvert$	0.855

Table 4. Quadrupole coupling constants [MHz] of some isothiocyanates.

	χ_{aa}	χ_{bb}	χ_{cc}
HNCS [7]	1.114 (26)	−0.530 (71)	−0.585 (71)
CH_3NCS [8]	1.90 (3)	–	–
CH_3CH_2NCS	1.873 (18)	−1.264 (26)	−0.609 (26)

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