Improved Rotational Constants and Dipole Moment and a Nuclear Quadrupole Coupling Analysis of 2-Cyanothiophene and Dipole Moment of 2-Cyanofurane

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Results of a microwave investigation of the molecules 2-Cyanothiophene and 2-Cyanofurane are reported. The microwave spectrum of 2-Cyanothiophene was examined in the frequency range of 13–40 GHz mainly to get a more accurate rotational constant A from the assignment of μ_b-transitions. From the resolved hyperfine structure due to nuclear quadrupole coupling of the ^{14}N-nucleus the quadrupole coupling constant $\chi_+ = \chi_{bb} + \chi_{cc}$ was determined for 2-Cyanothiophene. No information for χ_- was available from the measured transitions.

From Stark effect studies the dipole moments were determined for both molecules. The nuclear quadrupole coupling as a perturbation of the second order Stark effect was included in the Stark effect analysis.

Since the two molecules 2-Cyanothiophene and 2-Cyanofurane differ only by the isoelectronic ring atoms sulfur and oxygen they were investigated in parallel. In a preceding paper[1] we reported the rotational constants and the nuclear quadrupole coupling constants of 2-Cyanofurane. When our analysis of the spectrum of 2-Cyanothiophene was finished we noticed a publication of Avirah et al.[2] on the microwave spectrum of this compound. As our data are more complete and partly different they will be included in this publication.

Experimental

The spectra of both compounds were recorded in the region between 10 and 40 GHz with conventional microwave spectrometers using 30 and 100 kHz Stark modulation[3, 4]. For the assignment of the rotational spectrum of 2-Cyanothiophene radio frequency microwave double resonance (RFMWDR)[5] was of great help. The compounds were purchased from EGA-Chemie and used after destillation.

2-Cyanothiophene

The rotational spectrum exhibits rather strong μ_a- and weak μ_b-transitions. With the combined use of Stark-modulated and RFMWDR-spectroscopy, the initial assignment of the μ_a- and μ_b-transitions was possible. The measured transitions are given in

Table 1. Rotational transitions of the most abundant species of 2-Cyanothiophene in the vibrational ground state. Listed frequencies are intensity weighted center frequencies of the hyperfine multipletts. The transitions were used to calculate the constants of Table 2, ν_{calc} calculated with rigid rotor.

$J_{K_- K_+} - J'_{K'_- K'_+}$	ν_{obs} [MHz]	ν_{calc} [MHz]	$\Delta\nu$ [KHz]
$2_{02} - 3_{03}$	9362.60 *	9362.36	240
$2_{12} - 3_{13}$	8813.58 *	8813.39	190
$2_{11} - 3_{12}$	10184.15 *	10184.00	150
$3_{03} - 4_{04}$	12307.40 *	12307.14	260
$3_{13} - 4_{14}$	11708.57 *	11708.36	210
$3_{12} - 4_{13}$	13525.07	13525.12	50
$4_{04} - 5_{05}$	15136.84	15136.79	50
$4_{13} - 5_{14}$	16813.37	16813.32	50
$4_{14} - 5_{15}$	14573.02	14572.91	110
$4_{23} - 5_{24}$	15783.05	15782.91	140
$5_{14} - 6_{15}$	20027.36	20027.25	110
$5_{23} - 6_{24}$	20035.74	20035.57	170
$5_{32} - 6_{33}$	19340.40	19340.43	−30
$5_{33} - 6_{34}$	19215.81	19215.63	180
$5_{50} - 6_{51}$	19152.07	19151.94	130
$5_{51} - 6_{52}$	19152.07	19151.98	90
$6_{06} - 7_{07}$	20561.19	20561.16	30
$6_{25} - 7_{26}$	21908.81	21908.72	90
$6_{42} - 7_{43}$	22435.99	22436.06	−70
$6_{43} - 7_{44}$	22423.15	22423.34	−190
$7_{17} - 8_{18}$	22990.07	22989.79	280
$7_{44} - 8_{45}$	25673.16	25673.19	−30
$8_{26} - 9_{27}$	30451.29	30451.30	−10
$8_{44} - 9_{45}$	29015.26	29015.51	−250
$8_{45} - 9_{46}$	28934.62	28934.85	−270
$2_{20} - 3_{31}$	28583.18	28583.30	−120
$2_{21} - 3_{30}$	28626.49	28626.67	−180
$6_{06} - 7_{17}$	21199.66	21200.10	−440
$7_{07} - 8_{18}$	23628.45	23628.73	−280
$8_{36} - 8_{45}$	26594.39	26594.04	350
$8_{45} - 8_{54}$	34088.82	34088.90	−80

* Frequencies reported by Avirah[2].

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Table 2. Rotational and centrifugal distortion constants and correlation coefficients of 2-Cyanothiophene.

A	[MHz]	5402.387 ± 0.024	1.0						
B	[MHz]	1816.253 ± 0.005	−0.03	1.0					
C	[MHz]	1358.614 ± 0.005	−0.10	0.83	1.0				
Δ_J	[kHz]	-0.092 ± 0.044	−0.10	0.83	0.86	1.0			
Δ_{JK}	[kHz]	2.889 ± 0.080	0.20	−0.51	−0.57	−0.84	1.0		
Δ_K	[kHz]	-6.683 ± 0.740	0.90	−0.06	−0.12	−0.05	0.07	1.0	
δ_J	[kHz]	0.098 ± 0.004	0.22	0.18	−0.26	−0.11	0.27	0.14	1.0
δ_K	[kHz]	-4.852 ± 0.172	−0.43	−0.09	−0.03	−0.05	−0.13	−0.35	−0.65	1.0

Fitted with 39 transitions up to $J=17$, standard deviation 115 kHz.

Rigid rotor rotational constants

A	[MHz]	5402.469 ± 0.014	5401.35 ± 0.13 *
B	[MHz]	1816.231 ± 0.003	1816.26 ± 0.02 *
C	[MHz]	1358.588 ± 0.003	1358.64 ± 0.02 *

* Reported by Avirah et al. [2].

Table 1. Those given by Avirah et al. [2] are marked with an asterik. A search for μ_b-transitions proved to be rather tedious because of the low intensity and overlapping of lines.

The spectrum was analysed by the model of the centrifugal distorted rotor according to Watson [6]. Table 2 gives the rotational and centrifugal distortion constants and their correlation coefficients. For comparison with the results of Avirah et al. [2] lines with $J \leqq 9$ were used to fit the rotational constants of the rigid rotor. Our values differ by inclusion of μ_b-transitions, which determine the rotational constant A more reliably.

From the resolved quadrupole hyperfine structure due to the ^{14}N-nucleus given in Table 3, the quadrupole coupling constant $\chi_+ = \chi_{bb} + \chi_{cc}$ was determined to 4.04 ± 0.16 MHz. An extended search for lines sensitive to $\chi_- = \chi_{bb} - \chi_{cc}$ was unsuccessful.

A comparison of χ_+ of 2-Cyanothiophene with that of 2-Cyanofurane shows that both values are equal within the error limits. As further the orientation of the principal axis system of 2-Cyanothiophene (Fig. 1) is similar to that of 2-Cyanofurane (Fig. 1 [1]) the $\chi_- = 0.96$ of 2-Cyanofurane may be taken as a rough approximation also for 2-Cyanothiophene.

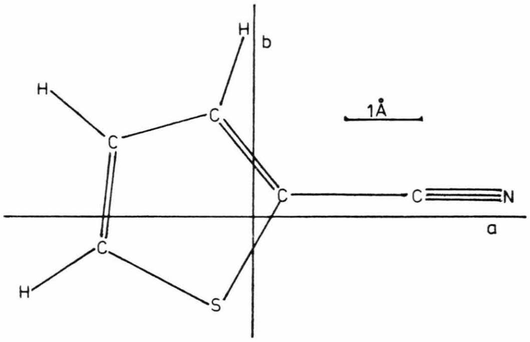


Fig. 1. Estimated structure of 2-Cyanothiophene.

Table 3. Hyperfine splittings (peak to peak frequency differences) used for the least squares fit of the quadrupole coupling constant χ_+ of 2-Cyanothiophene.

Rotational transitions	Hyperfine components	[MHz]	Splitting $\Delta\nu_{\text{obs}}$ [MHz]	Splitting $\Delta\nu_{\text{calc}}$ [MHz]
$J_{K_-K_+} - J'_{K'_-K'_+}$	$\nu_{F\to F'}$			
$7_{61} - 6_{60}$	$\nu_{8\to7}, \nu_{6\to5}$	22338.682	0.978	0.978
$7_{62} - 6_{61}$	$\nu_{7\to6}$	22337.704		
$9_{81} - 8_{81}$	$\nu_{10\to9}, \nu_{8\to7}$	28712.880	0.810	0.811
$9_{82} - 8_{81}$	$\nu_{9\to8}$	28712.070		
$10_{91} - 9_{90}$	$\nu_{11\to10}, \nu_{9\to8}$	31899.934	0.823	0.746
$10_{92} - 9_{91}$	$\nu_{10\to9}$	31899.111		
$11_{92} - 10_{91}$	$\nu_{12\to11}, \nu_{10\to9}$	35109.636	0.473	0.559
$11_{93} - 10_{92}$	$\nu_{11\to10}$	35109.163		
$11_{10,1} - 10_{10,0}$	$\nu_{12\to11}, \nu_{10\to9}$	35086.881	0.680	0.691
$11_{10,2} - 10_{10,1}$	$\nu_{11\to10}$	35086.201		

Fig. 2.

M_J, M_I	$-J, -I$	$-1, +1$	$0, 0$	$+1, -1$	J, I
$-J, -I$	$E_{\mathrm{St},\,\lvert M_J\rvert = J} + c$				
$-1, +1$		$E_{\mathrm{St},\,\lvert M_J\rvert = 1}$ $+a$	y	x	
$0, 0$		y	$E_{\mathrm{St},\,\lvert M_J\rvert = 0}$ $+b$	y	
$+1, -1$		x	y	$E_{\mathrm{St},\,\lvert M_J\rvert = 1}$ $+a$	
J, I					$E_{\mathrm{St},\,\lvert M_J\rvert = J} + c$

Stark-energy matrix of a J, τ level after application of second order Stark effect perturbation with added elements of $\mathcal{H}_Q$

$E_{\mathrm{St},\,M_J}$: Energy of the Stark level J, τ, M_J,

$a = \frac{1}{2}\,[J(J+1)-3]\,[I(I+1)-3]\cdot C(J,\tau,I)$,

$b = \frac{1}{2}\,J(J+1)\,I(I+1)\cdot C(J,\tau,I)$,

$c = \frac{1}{2}\,[J(J+1)-3\,J^2]\,[I(I+1)-3\,I^2]\cdot C(J,\tau,I)$,

$C(J,\tau,I) = (\sum_{g=a,b,c} \chi_{gg}\,\langle J,\tau \,\|\, J_g^2 \,\|\, J,\tau\rangle)/(J(2\,J-1)\,I(2\,I-1)\,(J+1)\,(2\,J+3))$.

a, b, c, x, y are the matrix elements of $\mathcal{H}_Q$ with

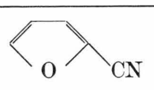
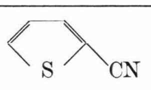
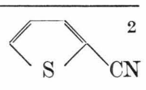
$x = \frac{3}{4}\,J(J+1)\,I(I+1)\cdot C(J,\tau,I)$,

$y = -\frac{3}{4}\,[J(J+1)\,I(I+1)]^{\frac{1}{2}}\cdot C(J,\tau,I)$,

Dipole Moments

The dipole moment components μ_a and μ_b were determined from second order Stark effect lines. Those of 2-Cyanothiophene were calculated by diagonalisation of the Stark energy matrix as the used transitions have very sensitive Stark satellites. Both dipole moment components were fitted together to the Stark effect satellites $|M_J| = 0, 1, 2, 3, 4$ of the transition $5_{32} - 6_{33}$ at 19340.46 MHz and to the satellites $|M_J| = 1, 2$ of the transition $4_{23} - 5_{24}$ at 15783.05 MHz. The electric field strength used for the measurement of the dipole moment was determined by calibration with OCS $J = 0 - 1$ [7]. The calculated dipole moments are listed in Table 4. The quoted errors include both the single standard error of the fit and the calibration uncertainty. The discrepancy between the values of Avirah et al. [2] and ours for 2-Cyanothiophene may indicate that the quoted error limits have to be considered with caution.

Table 4. Dipole moments.

			
μ_a[D]	4.51 ±0.02	4.47 ±0.03	4.51±0.02
μ_b[D]	0.901±0.005	0.736±0.008	0.86±0.04

The dipole moment components of 2-Cyanofurane were determined by a calculation, which applies first the second order Stark effect perturbation and second the perturbation by the ^{14}N-quadrupole coupling. If the strong field case is assumed with an effective decoupling of overall rotation and nuclear spin, all off-diagonal matrix elements with respect to M_J and M_I, the projection quantum numbers of the overall rotation and nuclear spin respectively, for a given rotational level denoted by J, τ, M_J and the nuclear spin I are small compared to the diagonal matrix elements by the second order Stark effect perturbation and the quadrupole coupling operator $\mathcal{H}_Q$ (compare Ref. [8]). However, it is not possible to apply second order perturbation theory again because the (M_J, M_I)-sublevels $(-1, +1)$ and $(+1, -1)$ are degenerate and connected by an off-diagonal element of $\mathcal{H}_Q$. The energy matrix for a given rotational level has the form indicated in Figure 2. Only the matrix elements involving the degenerate sublevels and $M_J, M_I = 0, 0$ are given completely. The degeneracy is removed by the application of the orthogonal transformation of Fig. 3 to the energy matrix of Figure. 2. The transforma-

Fig. 3. Transformation matrix.

$$\begin{pmatrix}
1 & & & & & & \\
 & \ddots & & & & & 0 \\
 & & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & & \\
 & & 0 & 1 & 0 & & \\
 & & \frac{1}{\sqrt{2}} & 0 & \frac{-1}{\sqrt{2}} & & \\
 & 0 & & & & \ddots & \\
 & & & & & & 1
\end{pmatrix}$$

Fig. 4. Transformed matrix of Figure 2.

$$\begin{array}{c|ccccc}
M_J, M_I & -J, -I & & & & J, I \\
\hline
-J, -I & E_{\mathrm{St}, |M_J| = J} + c & & & & \\
 & & E_{\mathrm{St}, |M_J| = 1} + a + x & \sqrt{2}\, y & 0 & \\
 & & \sqrt{2}\, y & E_{\mathrm{St}, |M_J| = 0} + b & 0 & \\
 & & 0 & 0 & E_{\mathrm{St}, |M_J| = 1} + a - x & \\
J, I & & & & & E_{\mathrm{St}, |M_J| = J} + c
\end{array}$$

tion leads to the energy matrix of Figure 4. The eigenvalues $E_{\mathrm{St}, |M_J| = 1} + a \pm x$ correspond to the mixed eigenfunctions

$$\frac{1}{\sqrt{2}} \{ | J, \tau, M_J = -1, I, M_I = 1 \rangle \pm | J, \tau, M_J = 1, I, M_I = -1 \rangle \} .$$

It should be mentioned that each rotational level J, τ, I is split into $(J+2)(2I+1)$ sublevels, which may be compared to the number of $(J+1)$ sublevels in the case without quadrupole effects.

From the result of a second order perturbation calculation applied to the matrix of Fig. 4 a better understanding of the partly complicated pattern of the Stark effect satellites is possible. One has to observe only that second order perturbation calculation is sufficient.

For 2-Cyanofurane two independent fits for μ_a and μ_b were made. The $|M_J| = 0$ satellite of the transition $4_{23} - 5_{24}$ at 18429.085 MHz has only less than 1% μ_a-contribution. For this reason it was possible to use an estimated μ_a-value of 4.5 Debye for the calculation of μ_b using the mentioned satellite. After having fixed the μ_b-value we determined μ_a from Stark satellites with $|M_J| = 0, 1, 2$ of the transition $3_{13} - 4_{14}$ at 14007.98 MHz (see Table 4).

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