Microwave Spectra of 3-Cyanothiophene-^{34}S and 3-Cyanothiophene-^{15}N and Partial r_0-structure

J. Wiese, R. Schwarz, and D. H. Sutter

Abteilung Chemische Physik im Institut für
physikalische Chemie der Christian-Albrechts-
Universität Kiel

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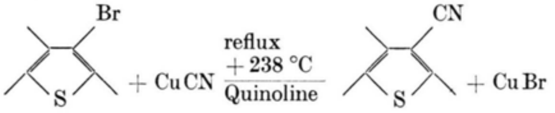
The rotational spectra of 3-Cyanothiophene-^{15}N and 3-Cyanothiophene-^{34}S were analyzed in the frequency range between 10 and 25 GHz.

A partial r_0-structure was fitted to the observed rotational constants. The cavity-Fourier-transform microwave spectrometer with pulsed supersonic nozzle beam gas injection is proposed as a promising tool to investigate the rotational spectra of vibrationally excited moleculs ($\tilde{\nu}_{\text{vib}} \gtrsim 800\ \text{cm}^{-1}$).

In the following we report the results of a microwave spectroscopic investigation of two additional isotopic species of 3-Cyanothiophene [1]). 3-Cyanothiophene was synthesized by reaction of 3-Bromothiophene with Copper (I) cyanide in Quinoline [2]:



The ^{34}S-species was investigated in natural abundance. The ^{15}N-species was synthesized using a ^{15}N enriched CuCN sample as reactant.

The spectra were recorded using a conventional 33 kHz Stark effect modulated microwave spectrometer [3, 4]. Typical recording conditions were: pressures close to 10 m Torr and temperatures close to 0 °C. At lower temperatures the vapour pressure in the cell quickly drops below the sensitivity threshold of our spectrometer (boiling point at 1 atmosphere: + 204 °C [5]).

In Table I we list the observed frequencies. Only the considerably more intense μ_a-spectra were assigned and only transitions with negligible centrifugal distortion and (for the ^{34}S-isotope) negligible ^{14}N hyperfine coupling [6] were measured under high resolution conditions. The rigid rotor rotational constants were fitted to the transition frequencies of Table 1 by the procedure described in [7]. They are given in Table 2. Also included in Table 2 are the rotational constants of the most abundant species [1].

Starting from the structures of Thiophene [8] for the ring and of Benzonitrile [9] for the CN-group, we tried to optimize bond distances and bond angles within the rigid rotor model. With experimental rotational constants of three isotopic species available, one might expect it to be possible to adjust up to six structural parameters (due to the planarity

Table 1. Observed rotational transitions of 3-Cyanothiophene-^{15}N and 3-Cyanothiophene-^{34}S in the vibrational ground state. All transitions show negligible centrifugal distortion shifts and (for the ^{34}S-species) negligible ^{14}N-quadrupole hyperfine coupling. They are compared to the corresponding frequencies calculated within the rigid rotor model from the rotational constants given in Table II.

$J_{K_-K_+} \rightarrow J'_{K_-'K_+'}$	ν_{exp}/MHz	ν_{calc}/MHz	$(\nu_{\text{exp}} - \nu_{\text{calc}})$/kHz
3-Cyanothiophene-^{15}N			
$3_{03} \rightarrow 4_{04}$	10 517.886	10 517.805	81
$3_{12} \rightarrow 4_{13}$	11 068.864	11 068.877	− 13
$3_{13} \rightarrow 4_{14}$	10 090.103	10 090.103	0
$3_{21} \rightarrow 4_{22}$	10 666.204	10 666.228	− 24
$3_{22} \rightarrow 4_{23}$	10 589.007	10 588.995	12
$6_{06} \rightarrow 7_{07}$	18 129.744	18 129.704	40
$6_{24} \rightarrow 7_{25}$	18 892.302	18 892.304	− 2
$6_{25} \rightarrow 7_{26}$	18 480.989	18 480.990	− 1
$7_{07} \rightarrow 8_{08}$	20 594.190	20 594.207	− 17
$7_{16} \rightarrow 8_{17}$	21 994.579	21 994.562	17
$7_{17} \rightarrow 8_{18}$	20 073.459	20 073.443	15
$7_{25} \rightarrow 8_{26}$	21 690.485	21 690.468	17
$7_{26} \rightarrow 8_{27}$	21 095.486	21 095.427	59
$8_{08} \rightarrow 9_{09}$	23 026.776	23 026.810	− 34
$8_{17} \rightarrow 9_{18}$	24 680.423	24 680.422	1
$8_{26} \rightarrow 9_{27}$	24 509.776	24 509.802	− 26
$8_{27} \rightarrow 9_{28}$	23 699.689	23 699.766	− 77
3-Cyanothiophene-^{34}S			
$4_{04} \rightarrow 5_{05}$	13 213.230	13 213.190	40
$4_{13} \rightarrow 5_{14}$	13 966.574	13 966.5166	58
$4_{14} \rightarrow 5_{15}$	12 712.925	12 712.982	− 57
$5_{14} \rightarrow 6_{15}$	16 734.449	16 734.399	50
$5_{15} \rightarrow 6_{16}$	15 235.434	15 235.364	70
$6_{06} \rightarrow 7_{07}$	18 289.946	18 289.915	31
$7_{07} \rightarrow 8_{08}$	20 771.237	20 771.160	77
$7_{16} \rightarrow 8_{17}$	22 220.048	22 219.941	107
$7_{17} \rightarrow 8_{18}$	20 250.964	20 250.791	173
$7_{26} \rightarrow 8_{27}$	21 300.806	21 300.827	− 21
$8_{08} \rightarrow 9_{09}$	23 219.705	23 220.012	−307
$8_{17} \rightarrow 9_{18}$	24 929.388	24 929.360	28
$8_{18} \rightarrow 9_{19}$	22 743.234	22 743.196	37
$8_{26} \rightarrow 9_{27}$	24 783.074	24 783.232	−158
$8_{27} \rightarrow 9_{28}$	23 928.745	23 928.772	− 27

Reprint requests to Prof. Dr. D. H. Sutter, Institut für Physikalische Chemie der Universität Kiel, Abt. Chemische Physik, Olshausenstraße 40–60, 2300 Kiel.

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Table 2. Rotational constants of 3-Cyanothiophene-^{15}N and 3-Cyanothiophene-^{34}S. They were obtained by a least squares fit to the transition frequencies listed in Table 1. Also listed are the rotational constants of the most abundant species [1], and the rotational constants calculated within the rigid rotor model from the structure given in Fig. 1. Since the A constants are largely determined by the weak μ_b-transitions, which could not be assigned for the ^{15}N- and ^{34}S-species, they could be determined only with reduced accuracy for these isotopic species and were not used in the fit of the structure.

All values in MHz

	3-Cyanothiophene [1]	3-Cyanothiophene-^{15}N	3-Cyanothiophene-^{34}S
A_{exp}	7115.180 (13)	7112.55 (308)	7067.131 (936)
B_{exp}	1491.299 (2)	1446.842 (3)	1463.308 (7)
C_{exp}	1232.535 (2)	1201.918 (3)	1211.308 (7)
A_{calc}	7115.103	(7112.038)	(7061.113)
B_{calc}	1491.069	1446.505	1463.476
C_{calc}	1232.733	1202.027	1212.231

condition each set of rotational constant is equivalent to only two equations of condition).

However, because of the high correlation, we finally decided to fit only the length of the C_2C_3 "double bond" adjacent to the Nitrile group together with the C_2-C_3-CN bond angle (see Figure 1). (This implied an implicit change of the "single bond" distance C_3-C_4). As compared to Thiophene the $C=C$ double bond adjacent to the CN group appears shortened (just as was found in Benzonitrile) and the adjacent $C-C$ single bond appears lengthened. The same trend towards the open chain geometry of a sp^2 hybridized Carbon atom at the C_3-position is seen in the C_2-C_3-CN bond angle which appears reduced by 1.5° and approaches the standard 120°-value. This trend towards an open chain geometry should – if real and not an artefact caused by the constraints imposed on the optimization procedure of the structural parameters – be accompanied by a correspondingly large drop in the nonlocal magnetic susceptibility component perpendicular to the ring [10] not yet measured so far.

To confirm and improve the structure presented in Fig. 1 more isotopic species must be studied, if possible also in excited vibrational states so as to make a complete equilibrium structure determination possible. While the latter will still involve ex-

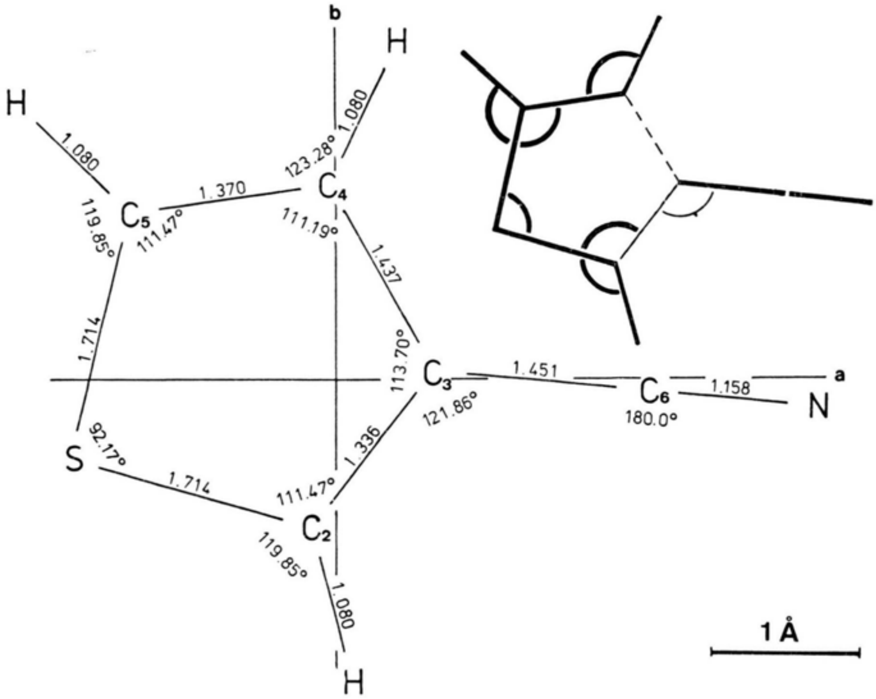

Fig. 1. Optimized structure of 3-Cyanothiophene resulting from a fit of the C_2C_3 bond distance and the C_2-C_3-CN bond angle to the experimental rotational constants (see Table 2). (The $C_2-C_3-C_4$ bond angle and the C_3C_4 bond distance are changed implicitely). Bold face bonds and bondangles in the insert indicate structural parameters that were kept fixed to their corresponding values in Thiophene (ring) and Benzonitrile (CN-group).

tensive work for larger molecules such as 3-Cyanothiophene, r_e-structure determinations should be considerably simplified in the near future by the use of microwave Fourier transform spectrometers combined with pulsed nozzle beams [11]. In such a spectrometer, presently exclusively used to study van der Waals molecules, rotational temperatures are drastically cooled down to approximately 10 K while vibrational temperatures should be reduced by a far lesser extent [12], leaving considerable Boltzmann populations in the excited vibrational states. With rotational population differences in the lowest J states of the vibrationally excited molecules increased by several orders of magnitude, their signals should be easily detectable even in cases where a sizable amount of dimers is present in the beam. We therefore expect that the derivation of equilibrium values for those molecular parameters which can be determined by rotational spectroscopy, will become feasible for a much larger class of molecules.

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