Rotational Spectrum of Methylcyanoacetylene
A New Millimeter Wave Spectrometer

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The ground state rotational spectrum of methylcyanoacetylene, CH_3CCCN, has been observed between 8 and 90 GHz, yielding precise rotational constants and a determination of the nuclear hyperfine costant $eqQ = -4.0 \pm 0.2$ MHz. The millimeter wave spectra (70 – 90 GHz) were obtained with a newly constructed spectrometer, employing a synthesizer – controlled reflex klystron as source.

I. Indroduction

Methylcyanoacetylene, CH_3CCCN, as a member of the unsaturated carbon chain molecules could be of potential astrophysical interest. Being related to the abundant interstellar molecule HCCCN, it bears similar chemical characteristics, in particular that it also can be generated in a radio-frequency discharge burning in a methylacetylene (CH_3CCH)/hydrogen cyanide (HCN) gas mixture as has been demonstrated earlier [1]. The present new data, however, have been obtained from a chemically prepared sample**.

Although the ground state microwave spectrum of methylcyanoacetylene has been reported as early as 1954 by Sheridan and Thomas [2], there is no further mention of this molecule in the literature until the recent discharge experiments [1] and now the publication of the ground state millimeter wave spectrum of this molecule by Moïses et al. [3]. However several aspects of the rotational spectrum of CH_3CCCN have not yet been treated with the accuracy desired for astrophysical purposes: there is no reliable determination of the ^{14}N-nuclear quadrupole constant, several ground state transitions at low and medium J values have not been measured and finally there exist no measurements of rotational transitions in vibrationally excited bending states.

The purpose of the present contribution is twofold: i) to report supplemental measurements on the grond state of CH_3CCCN, which have been carried out with a newly constructed millimeter wave spectrometer and ii) to discuss briefly the essential design features of the Cologne millimeter wave spectrometer employed in the present measurements. Although in the present measurements many lines arising from the molecules in excited bending vibrational states have been observed, both in the millimeter and microwave region, they will not be reported here, pending their detailed analysis.

II. Measurements

The measurement of several new millimeter wave transitions were complemented by observation of rotational transitions in the microwave region, particularly to obtain a reliable determination of the ^{14}N-nuclear quadrupole coupling constant, which is of importance to the possible identification of narrow interstellar CH_3CCCN lines at low and medium J values, arising from dark clouds – such as TMC1.

The measured CH_3CCCN transitions at low J are remarkably broad, probably caused by the combined effects of K-structure, nuclear hyperfine structure and contribution from the remaining pressure broadening due to the large dipole moment. Therefore only the observed profile of the $J = 2 - 1$ transition could be used for a reliable eqQ determination. Our new data are summarized in Table 1.

III. Millimeter wave spectrometer

The new Cologne millimeter wave spectrometer is of the free space type and is similar to the one in Giessen discussed by Winnewisser et al. [4] and

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Table 1. Observed Transitions and Fitted Parameters.

$(J+1, K) - (J, K)$	f_{obs}/MHz	f_{calc}/MHz	$f_{obs}-f_{calc}$/ kHz
(2, 0) − (1, 0)	8 263.000[a]	8 262.9505	49.5
(3, 0) − (2, 0)	12 394.360[b]	12 394.4201	− 60.1
(5, 0) − (4, 0)	20 657.325[b]	20 657.3369	− 11.9
(6, 0) − (5, 0)	24 788.200[c]	24 788.7795	− 579.5
(18, 0) − (17, 0)	74 364.385	74 364.3986	− 13.6
(18, 1) − (17, 1)	74 363.658	74 363.6823	− 24.3
(18, 2) − (17, 2)	74 361.516	74 361.5333	− 17.3
(18, 3) − (17, 3)	74 357.918	74 357.9522	− 34.2
(18, 4) − (17, 4)	74 352.922	74 352.9398	− 17.8
(18, 5) − (17, 5)	74 346.462	74 346.4972	− 35.2
(18, 6) − (17, 6)	74 338.563	74 338.6258	− 62.8
(18, 7) − (17, 7)	74 329.322	74 329.3273	− 5.3
(18, 8) − (17, 8)	74 318.571	74 318.6038	− 32.8
(18, 9) − (17, 9)	74 306.480	74 306.4576	22.4
(18, 10) − (17, 10)	74 292.936	74 292.8915	44.5
(20, 0) − (19, 0)	82 626.518	82 626.5408	− 22.8
(20, 1) − (19, 1)	82 625.760	82 625.7450	15.0
(20, 2) − (19, 2)	82 623.380	82 623.3580	22.0
(20, 3) − (19, 3)	82 619.393	82 619.3802	12.8
(20, 4) − (19, 4)	82 613.790	82 613.8124	− 22.4
(20, 5) − (19, 5)	82 606.740	82 606.6560	84.0
(20, 6) − (19, 6)	82 597.987	82 597.9125	74.5
(20, 7) − (19, 7)	82 587.620	82 587.5839	36.1
(20, 8) − (19, 8)	82 575.645	82 575.6723	− 27.3
(20, 9) − (19, 9)	82 562.150	82 562.1805	− 30.5
(21. 0) − (20, 0)	86 757.524	86 757.5456	− 21.6
(21, 1) − (20, 1)	86 756.698	86 756.7102	− 12.2
(21, 2) − (20, 2)	86 754.171	86 754.2042	− 33.2
(21, 3) − (20, 3)	86 750.040	86 750.0281	11.9
(21, 4) − (20, 4)	86 744.220	86 744.1829	37.1
(21, 5) − (20, 5)	86 736.666	86 736.6699	− 3.9
(21, 6) − (20, 6)	86 727.490	86 727.4907	− 0.7
(21, 7) − (20, 7)	86 716.618	86 716.6473	− 29.3
(21, 8) − (20, 8)	86 704.155	86 704.1421	12.9
(21, 9) − (20, 9)	86 689.970	86 689.9779	− 7.9
(21, 10) − (20, 10)	86 674.125	86 674.1578	− 32.8

[a] Line center is obtained by analyzing the hyperfine splittings. The $K = 0$ and 1 lines are overlapping each other.
[b] Higher K lines are overlapping. 25 times less weighted.
[c] Higher K lines are overlapping. Not used in the fit. Number of lines fitted: 100, Standard deviation: 35.0 kHz.
Fitted parameters:

B	= 2065.73836 (18) MHz	H_{KJ} =	0.365 (11) Hz
D_{JK} =	19.9242 (28) kHz	H_{JK} =	0.03793 (32) Hz
D_J =	93.550 (56) Hz	H_J =	− 0.0000087 (61) Hz

Helms et al. [5]. The particular difference between the Cologne spectrometer and the Giessen spectrometer lies in the frequency control system of the reflex klystron. Whereas the Giessen spectrometer employs a special sweep stabilizer to control the free running reflex klystron, the present system (Fig. 1) employs a phase-locked millimeter wave klystron, the frequency of which is controlled by a digital synthesizer, both in the video- and in the lock-in-mode (source frequency modulation with a sine wave and detection with a lock-in-amplifier). This phase-stabilized klystron output is fed into the free space absorption cell via a corrugated horn antenna and a set of teflon lenses to collimate the beam. The glass cell has a length of about 1.8 m and a diameter of 10 cm. The signal received by a detector horn is demodulated in a wave guide detector with following lock-in-amplifier. A microprocessor system controls the sweep and generates frequency markers on the dual pen recorder.

The phase-lock system is identical to the one which will be used in the millimeter wave receivers of the Cologne 3 m – millimeter wave radiotelescope, which is presently under construction at our institute [6]. The block diagram of the PLL (phase-locked loop) is presented in Figure 2. The reflex klystron is phase-locked by adding to the reflector voltage a correction voltage being proportional to the phase and frequency error of the klystron signal. A small part of the klystron output power is mixed with the n-th harmonic of a highly stabilized frequency synthesizer to obtain an IF-signal near 400 MHz, which contains a possible phase or frequency drift of the klystron. The IF-signal is levelled to a constant amplitude and then multiplied in a phase- and frequency-difference detector with a second 400 MHz reference signal, derived from another frequency synthesizer in the lock-in-mode or a sweeper in the video-mode. The resulting phase- and frequency-difference signals are used to correct the klystron reflector voltage. The servo amplifier in the reflector line consists of two paths: i) the integral path which is coupled to the klystron reflector circuitry by an opto-coupler and ii) the fast proportional path linked by a capacitor. The coarse adjustment of the klystron frequency is done by the slow integral path, whereas the fine adjustment i.e. the phase-locking is done by the proportional path. If the frequency-difference signal is zero in the locked mode, the phase-difference signal dominates in the servo loop and provides continuous locking of the klystron to the 400 MHz reference source.

By sweeping the frequency-modulated reference source (lock-in-mode) at 400 MHz by an amount of ± 50 MHz, the klystron will follow instantaneously and its frequency is known exactly at any time as the center frequency of the modulated signal. The video-mode (10 ms/sweep) is presently used for adjusting the spectrometer.

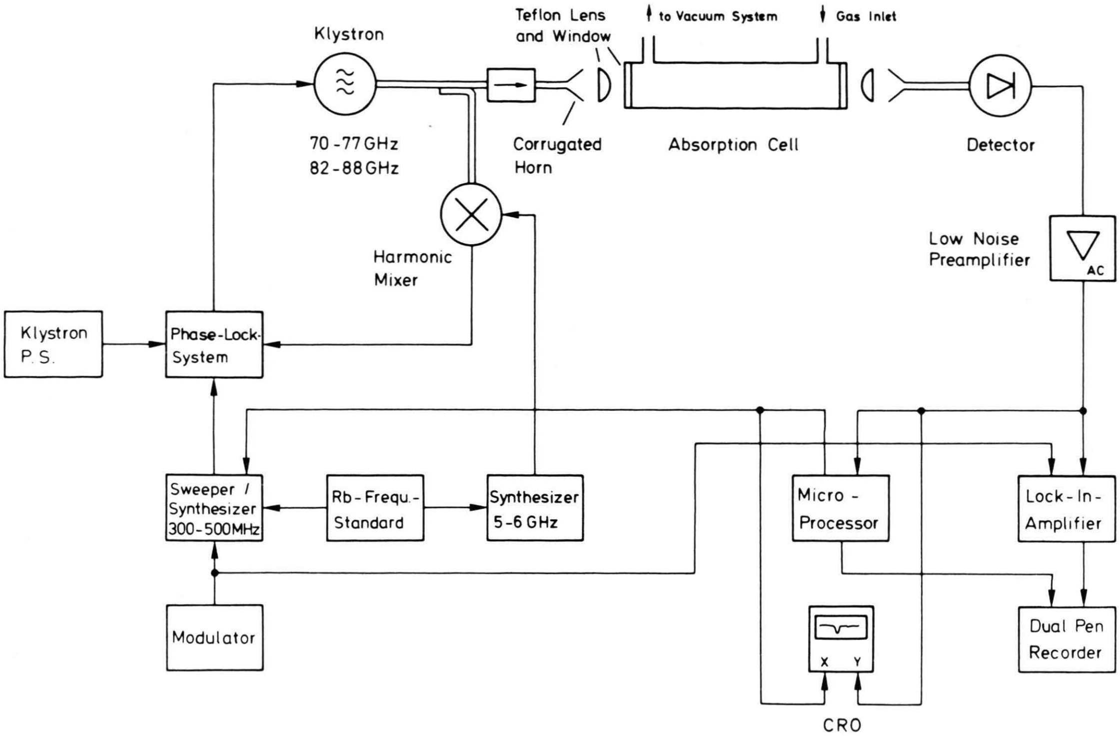

Fig. 1. Block diagram of the millimeter wave spectrometer. The spectrometer is of the free space type. The mm-wave signal is frequency – modulated and detected at the second harmonic of the modulation frequency.

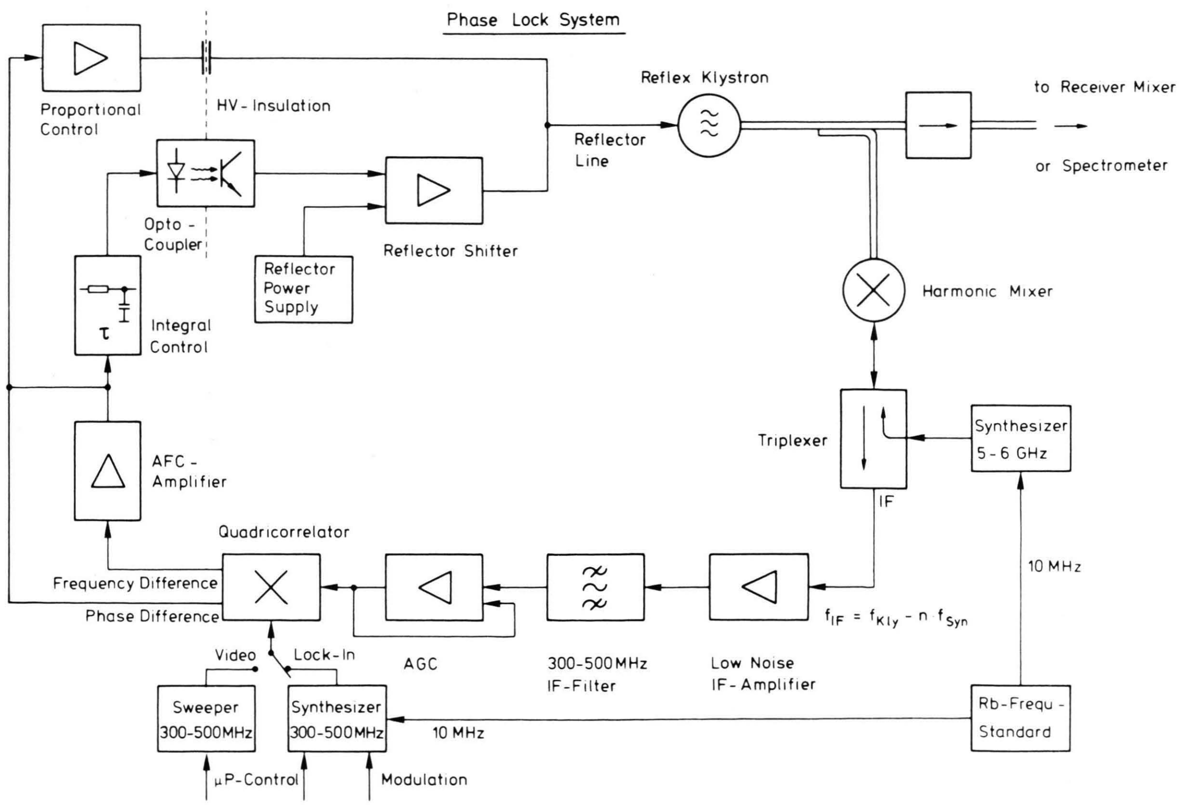

Fig. 2. Schematic diagram of the phase-locked loop (PLL). The PLL locks a reflex klystron to a stable reference signal. The system is also used as local oscillator in the receivers of the Cologne 3 m – millimeter radiotelescope.

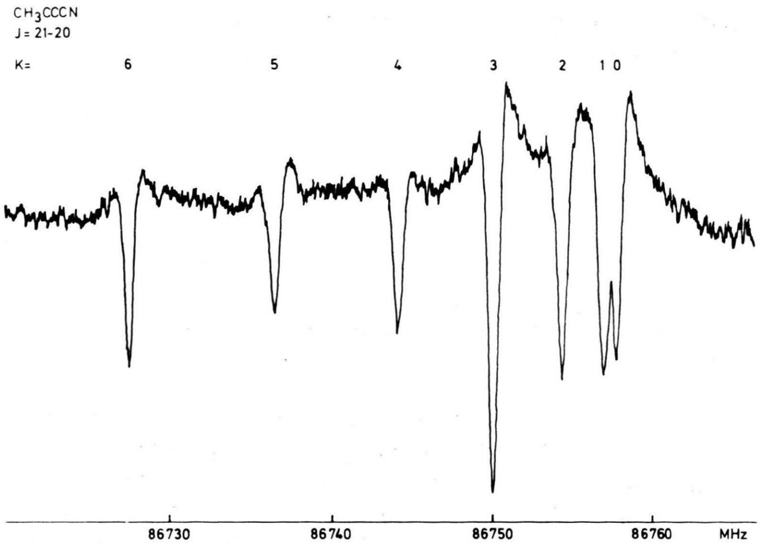

Fig. 3. Rotational spectrum of CH_3-CCCN at 86 GHz. The spectrum has been measured in the lock-in-mode, sweeping the klystron with a rate of 100 kHz/s.

The millimeter wave spectrometer will be further improved in due course by use of a frequency multiplier and a He-cooled InSb-detector to allow measurements in the submillimeter wave region. A microprocessor program for signal averaging in the video-mode will improve the sensitivity.

IV. Results and discussion

The mm-wave-data presented in Table 1 and the recording shown in Fig. 3 were obtained in the lock-in-mode, whereas the lines between 8 and 26 GHz have been measured with the Stark-modulation – Hewlett-Packard spectrometer [7], located at the University of Giessen.

The observed data have been fitted to the standard expression for rotational transition frequencies of symmetric rotors including the D- and H-centrifugal distortion terms. The molecular parameters thus derived are listed in Table 1. For astrophysical reference the quoted constants are reported with sufficient significant digits to allow the calculated spectra to reproduce the best fit to the Moïses et al. [3] and our data.

The value for the ^{14}N-nuclear quadrupole constant has been obtained by fitting the position of the 10 strongest hyperfine components (see [8]) to the observed profile of the $J = 2 - 1$ transition. The result is: $eqQ = -4.0 \pm 0.2$ MHz

It may be noticed that the frequency of the $J = 21 - 20$, $K = 3$ line of CH_3CCCN at 86.750 GHz coincides within the error limits to one of the published unidentified interstellar lines [9]. A possible identification would require the interstellar detection of other lines of CH_3CCCN, which are now precisely known.

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