Diode Laser Spectrum of HCCCN near 5 μm *

The Hot Band

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Two hot bands associated with the ν_3 vibration-rotation band of cyanoacetylene, HC_3N, have been measured with a diode laser spectrometer in the 2060–2100 cm^{-1} range. Since the width of the observed lines is essentially determined by Doppler broadening, the splitting of the hot band rovibrational transitions due to l-type doubling could be resolved and was assigned. Improved spectral parameters were obtained, including the anharmonicity parameters.

Introduction

In a recent study we have reported on the ν_3 vibration-rotation band (band center at 2079.3 cm^{-1}) of cyanoacetylene HC_3N. The spectra have been measured to an accuracy of better than ± 0.005 cm^{-1} using a newly constructed diode laser spectrometer [1]. The study of carbon chain molecules with high resolution is part of a program which we have started with the aim to measure and interpret the high resolution infrared spectra of molecules of astrophysical interest. The linear molecule cyanoacetylene, HC_3N, is next to HCN the lowest member of the remarkable carbon chain molecules HC_5N, HC_7N and HC_9N which all have been detected in interstellar and circumstellar molecular clouds by radio astronomy [2–5]. Therefore, HC_3N was chosen as the first molecule to be investigated by diode laser spectroscopy. HC_3N as a five-atomic linear molecule exhibits 7 infrared active fundamental vibrations. Four are bond stretching vibrations of species Σ^+ and three are doubly degenerate bending vibrations of species Π. Table 1 summarizes the present observational status of the measured fundamental frequencies of HC_3N. It indicates that the ν_3 vibration-rotation spectra near 5 μm measured by diode laser techniques constitute the highest resolution infrared measurements made to date on this molecule.

In addition to the ν_3 vibration-rotation transitions we succeeded for the first time to resolve several series of narrowly spaced doublets. Two of these series could be identified as the hot bands $\nu_3 + \nu_7 - \nu_7$ and $\nu_3 + 2\nu_7 - 2\nu_7$ whose rotational assignment will be discussed in the present communication. A refinement of the spectroscopic parameters of the ν_3 fundamental band reported earlier (1) will also be included. Thus the present paper is intended as a continuation of our earlier discussion of the diode laser spectrum of HCCCN.

Table 1. Fundamental frequencies of HC_3N.

	Assignment	Band origin (cm^{-1})	Ref.
1	CH-stretch	3327.372 (3)	a
2	CN-stretch	2273.996 (3)	a
3	C–C-stretch	2079.306 (3)	a
		2079.306 (2)	b
4	C–C-stretch	863.5 (10)	a
5	HC–C-bend	663.209 (12)	a
6	C–C–N-bend	498.5 (10)	a
7	C–C–C-bend	222.402 (15)	a

Numbers in parenthesis are 3 times standard deviation.
[a] Taken from Ref. [9]; resolution 0.025–0.050 cm^{-1}.
[b] Present work.

Experimental

The measurements were made with a newly constructed spectrometer whose essential features were briefly described by Yamada et al. [1]. Figure 1 presents a block diagram of the simplest version of the diode laser spectrometer. The radiation produced in the lead salt semiconductor was passed through a 150 cm long glass sample tube and then redirected on to the entrance slit of the grating mode selector. The laser emission of the diode is often multi-moded. The desired single mode of the diode-laser emission is selected by a grating mono-

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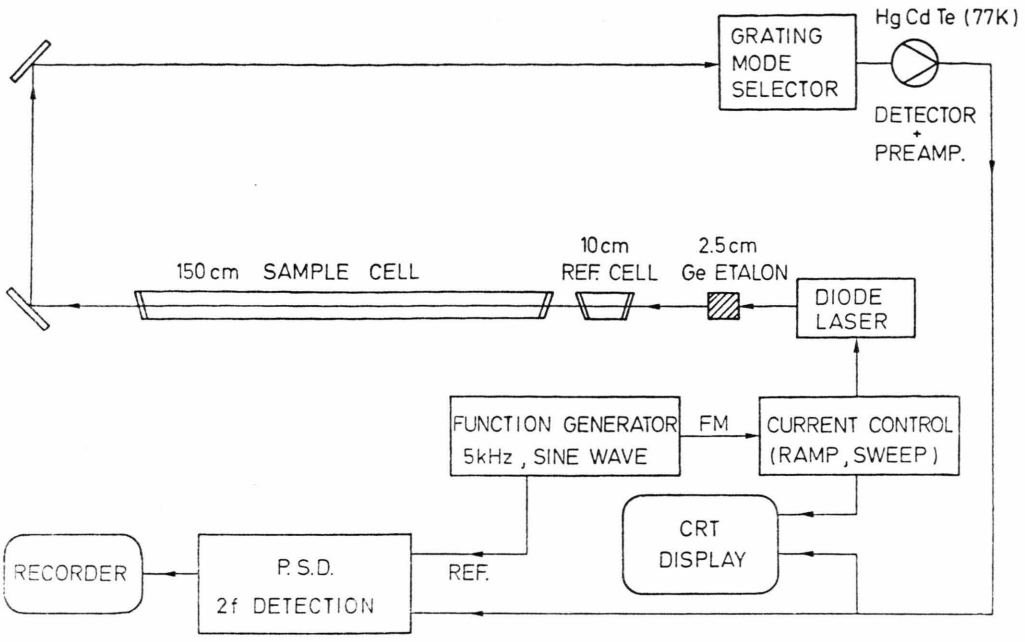

Fig. 1. Block diagram of the diode laser spectrometer. The reference cell and the germanium etalon can be removed from the diode laser beam.

chromator. Its single-moded light output is focused onto a liquid nitrogen cooled HgCdTe-detector. The reference cell and the germanium etalon can be placed simultaneously into the beam and are being used for calibration of the wave-numbers. The reference cell contains a gas which supplies us the absolute wavenumber scale. In the present case it was CO, whose rovibrational transitions have been measured very precisely by Guelachvili [6]. The Fabry-Perot fringes of the germanium etalon are used for relative interpolation between the precisely known CO-lines. The free spectral range of the etalon was 0.05 cm^{-1}.

The diode laser was source-modulated by a 5 kHz sinewave and the detector signal output was synchronously demodulated with a phase sensitive detecting system at twice the modulation frequency, thus displaying the second derivative form of the absorption lines. All spectra were recorded in this fashion. The resolving power of the diode laser spectrometer was essentially limited by the Doppler broadening of the rovibrational transitions. The observed linewidth, typically in order of 0.005 cm^{-1} (fullwidth at half maximum), contains a contribution from pressure broadening due to the sample pressure of a few Torr.

Spectrum: Assignment and Analysis

The band of the C≡C stretching fundamental ν_3 appears in the 5 μm region and is accompanied by rather intense hot bands due to the thermal excitation of the lowest bending vibrations. It is the purpose of this contribution to discuss the assignments of the hot bands from $v_7 = 1$ and 2 states. For the first time the l-type components have clearly been resolved and thus a detailed rotational analysis becomes possible.

The most intense transitions of the recorded spectra have been assigned to the ν_3 fundamental band, which are $\Sigma - \Sigma(l = 0)$ transitions, with strong R- and P-branch transitions. A small part of the spectrum has been published earlier by Yamada et al. [1] and is here reproduced once more as Figure 2. In the earlier publication the three most intense, successive and nearly equidistant lines of the P-branch were assigned to the fundamental band of ν_3. The P(17) CO line has been used as an absolute wavenumber standard. However, interdispersed are regularly spaced but narrowly split doublets, which we reported as arising from the hot bands [1]. Two sets of hot bands have been identified; the narrowly spaced, medium intense transitions are assigned to

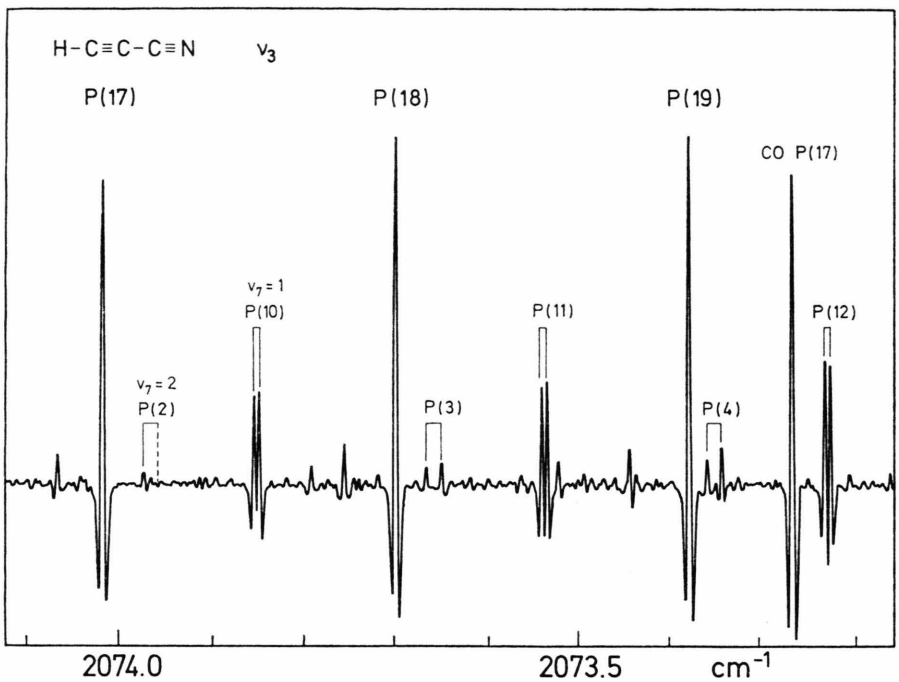

Fig. 2. High resolution diode laser spectrum of the ν_3 vibration-rotation spectrum of HC_3N. The three successive strong lines are members of the P-branch of $v_3 = 1 - 0$. The spectrum is identical to the one displayed in Ref. [1] as Fig. 1, contains, however, the new assignment of the hot bands. The sequences of weaker lines split into doublets by l-type resonance have been assigned to P-branch transition of the v_3, $v_7 = 1,1 - 0,1$ and v_3, $v_7 = 1,2 - 0,2$ hot bands. The spectrum has been recorded employing frequency modulation and has been displayed in second derivative form. Slight reflection of laser power back into the laser causes weak energy modulation producing non systematic noise in the baseline. The P(17) CO line served as calibration standard.

the band $\nu_3 + \nu_7 - \nu_7$. The weaker set of doublets but more widely spaced and with different intensities of the individual components arise from the band $\nu_3 + 2\nu_7 - 2\nu_7$.

The $\nu_3 + \nu_7 - \nu_7$ hot band consists of Π-Π transitions which form P, Q and R-branches with $l = 1$. Due to the limited tunability of the laser diode only the P- and R-branches could be observed. Figure 2 presents the rotational assignment for three successive rovibrational transitions of the P-branch of $\nu_3 + \nu_7 - \nu_7$. Figure 2 also shows the rotational assignment of the second hot band $\nu_3 + 2\nu_7 - 2\nu_7$. The weaker of the two components belongs to a Σ-$\Sigma(l = 0)$ band whereas the stronger component (about twice the intensity) arises from the Δ-$\Delta(l = 2)$ band. Since the expected l-type doubling of the latter band has not been resolved with the present system, the apparent line intensity of this component is doubled. Although the Δ-Δ band consists of P-, Q-, and R-branches as well, only P- and R-branch transitions were observed. The diode laser could not be tuned to the location of the Q-branch. Two representative high dispersion scans are shown in Fig. 3 and 4. From the entire spectrum scanned, both figures contain small selected regions of the P- and R-branch together with the wavelength calibration lines of CO. They were chosen on the basis to show at least two successive rotational lines of each of the bands, i.e. the ν_3 fundamental and the two hot bands.

The rotational assignment of the hot bands was obtained following the method applied for the ν_3 fundamental band, which has been discussed in detail by Yamada et al. [1]. This iterative procedure can be used generally for all those cases where a number of rotational lines can be measured from P-, or R-branches, but where the region of the band center itself is experimentally not accessible. These cases are often met in diode laser spectroscopy. The assignment method then relies on the fact that at least one of the parameters has to be known to sufficient high accuracy from other independent

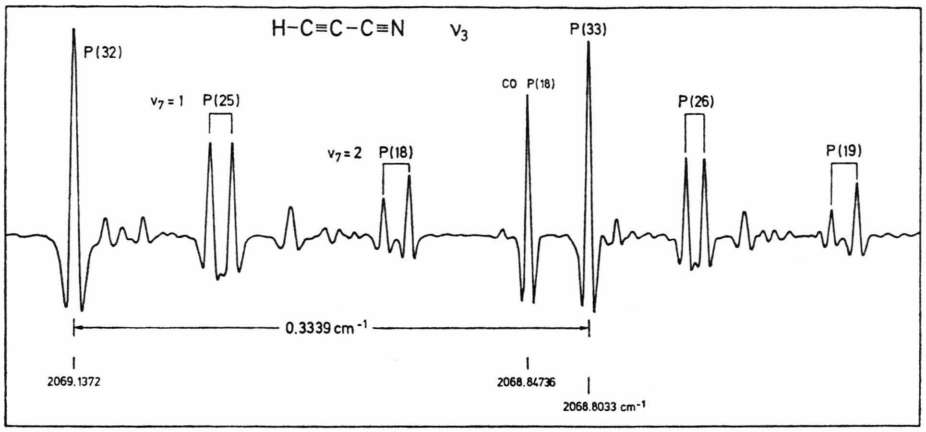

Fig. 3. High dispersion run of a small portion of the P-branch section of the ν_3 vibration-rotation spectrum near 2069 cm^{-1}. This section has been selected to display two successive rovibrational transitions of the fundamental band v_3, $v_7 = 1,0 - 0,0$ and the hot bands v_3, $v_7 = 1,1 - 0,1$ and $1,2 - 0,2$. The P(18) CO line has been used as calibration standard in this section of the spectrum.

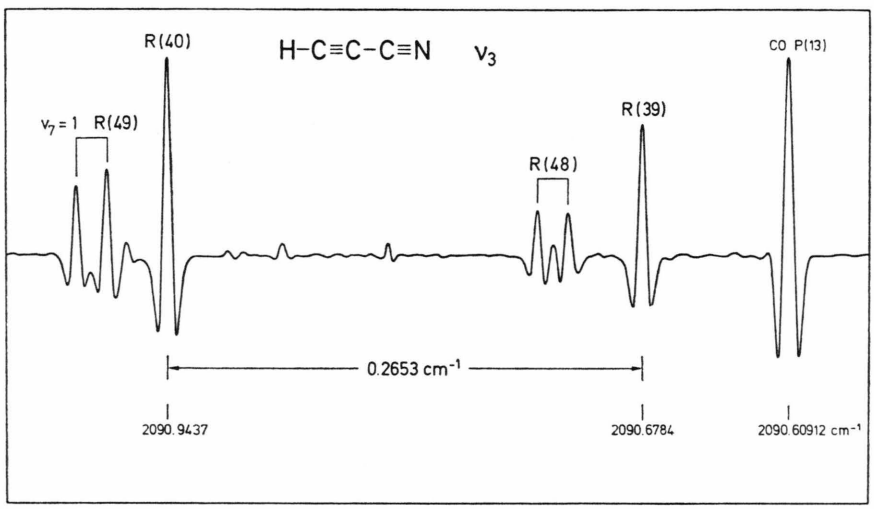

Fig. 4. High dispersion run of a selected portion of the R-branch of HC_3N near 2090.8 cm^{-1}. This section presents two successive rovibrational transitions of the ν_3 fundamental band and the hot band v_3, $v_7 = 1,1 - 0,1$. The P(13) CO line was used as calibration standard.

measurements. In the present case the assignment of the measured hot band transitions were adjusted such that consistency in the lower state constants was obtained with those which are accurately known from microwave spectroscopy. An independent check on the assignment reached this way comes from the fact that the rovibrational transition P(2) in the Δ-Δ ($l = 2$) band is missing (see Fig. 2) which is expected from the requirement that the total angular momentum J and the vibrational angular momentum l satisfy the relation. $J \geqq l$.

The measured transition-wavenumbers were analyzed by a least-squares fit using the following conventional equation:

$$\nu_m = \nu_0 + (B' + B'')\,m + (B' - B'' - D' + D'')\,m^2 - 2(D' + D'')\,m^3 - (D' - D'')\,m^4 \quad (1)$$

where ν_0 is the band center including the $-Bl^2$ contributions, B and D are the rotational and centrifugal distortion constants, respectively. The upper and lower state are designated as usual by

Table 2. Transition wavenumbers of the $\nu_3+\nu_7-\nu_7$ band of HCCCN in cm^{-1}.

J'	J''	$l=1^e$		$l=1^f$	
		calc.[a]	(o−c) $\times 10^4$	calc.	(o−c) $\times 10^4$
26	27	2068.4044	1	2068.3906	− 6
25	26	2068.7324	5	2068.7191	6
24	25	2069.0595	13	2069.0468	14
23	24	2069.3857	28	2069.3735	31
22	23	2069.7110	49	2069.6994	46
14	15	2072.2807	10	2072.2732	19
13	14	2072.5978	−19	2072.5908	−14
12	13	2072.9140	−19	2072.9075	−18
11	12	2073.2292	− 3	2073.2223	− 2
10	11	2073.5436	6	2073.5381	6
9	10	2073.8570	20	2073.8520	18
2	1	2077.5465	− 1	2077.5469	− 5
3	2	2077.8479	14	2077.8488	5
15	14	2081.3931	−56	2081.3987	−52
16	15	2081.6825	− 8	2081.6884	− 8
17	16	2081.9710	−19	2081.9773	−27
18	17	2082.2586	1	2082.2652	11
46	45	2089.9351	−11	2089.9493	−15
47	46	2090.1959	−13	2090.2104	−15
48	47	2090.4559	− 5	2090.4705	− 8
49	48	2090.7149	− 4	2090.7297	3
50	49	2090.9730	− 7	2090.9880	0
51	50	2091.2302	−15	2091.2454	−13
52	51	2091.4865	−16	2091.5019	−17
53	52	2091.7419	−10	2091.7575	−16
55	54	2092.2500	9	2092.2659	12
57	56	2092.7545	23	2092.7707	11
58	57	2093.0054	29	2093.0217	26
59	58	2093.2554	24	2093.2719	26
60	59	2093.5045	16	2093.5211	17
61	60	2093.7527	4	2093.7695	8
62	61	2094.0000	1	2094.0169	− 6
63	62	2094.2465	−22	2094.2635	−15
64	63	2094.4920	−22	2094.5091	−21
	[b]	0.0020		0.0020	

[a] Calculated wavenumbers.
[b] Standard deviation of the fit.
Note: The *l*-type doublets are labeled by superscript e and f. This represents transitions from lower to lower and upper to upper *l*-type component respectively.

Table 3. Transition wavenumbers of the $\nu_3+2\nu_7-2\nu_7$ band of HCCCN in cm^{-1}.

J'	J''	$l=0$		$l=2$	
		calc.[a]	o − c	calc.[b]	o − c
18	19	2068.6308	−21	2068.6129	−20
17	18	2068.9525	0	2068.9347	−10
16	17	2069.2734	26	2069.2557	10
15	16	2069.5933	30	2069.5758	36
6	7	2072.4327	−15	—	
5	6	—		2072.7269	3
4	5	—		2073.0370	− 4
3	4	2073.3627	− 3	2073.3461	− 6
2	3	2073.6709	6	2073.6543	− 7
1	2	2073.9782	7	(Missing)	
9	8	2077.2969	−27	2077.2800	−37
10	9	2077.5930	3	2077.5761	29
11	10	2077.8882	9	2077.8713	19
23	22	2081.3589	−35	2081.3426	−29
24	23	2081.6422	− 8	2081.6261	−13
25	24	2081.9246	17	2081.9088	16
26	25	2082.2061	10	2082.1906	13
[c]		0.0020		0.0022	

[a] Calculated wavenumbers.
[b] The *l*-type doublets were not resolved. The wavenumbers for e components are listed here, because the e—f splittings are very small; for example, the e—f splitting of R (25) lines is calculated to be 0.003 cm^{-1}.
[c] Standard deviation of the fit.

prime and double prime. The numbers m take on the following values: $m=-J$ for the P(J) and $m=J+1$ for R(J) transitions.

In the final fit the lower state constants, B'' and D'', were fixed to the highly precise values obtained by microwave spectroscopy [7, 8].

Table 2 and Table 3 contain the observed transitions of the two hot bands $\nu_3+\nu_7-\nu_7$ and $\nu_3+2\nu_7-2\nu_7$; the calculated wavenumbers based on the best fit parameters are given together with the observed-calculated values.

v_3'	v_7'	v_3''	v_7''	ν_0	B' / B''	$D'\times 10^7$ / D''
1	0°	0	0°	2079.30606 (71)[c]	0.1512747 (13)	0.1712 (44)
					0.151740204 (fixed)[a]	0.18116 (fixed)[a]
1	1^{1e}	0	1^{1e}	2076.94077 (63)	0.1516511 (10)	0.1712 (27)
					0.15211306 (fixed)[b]	0.1839 (fixed)[b]
1	1^{1f}	0	1^{1f}	2076.94039 (62)	0.1518668 (10)	0.1788 (26)
					0.15233129 (fixed)[b]	0.1920 (fixed)[b]
1	2°	0	2°	2074.58991 (99)	0.1522418 (83)	0.343 (119)
					0.15270465 (fixed)[b]	0.4104 (fixed)[b]
1	2^{2e}	0	2^{2e}	2074.57334 (112)	0.1522358 (94)	0.079 (135)
					0.15270265 (fixed)[b]	0.1970 (fixed)[b]
1	2^{2f}	0	2^{2f}	2074.57319 (113)	0.1522399 (95)	− 0.040 (136)
					0.15270269 (fixed)[b]	− 0.0118 (fixed)[b]

Table 4. Spectroscopic Parameters of HC_3N in cm^{-1}.

[a] Creswell et al. (2).
[b] Calculated from the microwave data of Mallison and Zafra (3).
[c] Numbers in parenthesis are one standard deviations.

Since the effect of centrifugal distortion was neglected in the earlier analysis of the ν_3 fundamental band (1), we have reanalyzed the data of the fundamental once more by using Equation [1]. The obtained spectroscopic parameters of the hot bands as well as the fundamental band are listed in Table 3.

Vibrational Analysis

The newly obtained experimental data were precise and extensive enough to derive from the present values of the band centers several anharmonicity parameters. The vibrational energy expression used is of the form

$$G_0(v) = \sum \omega_i^0 v_i + \sum x_{ij}^0 v_i v_j + \sum y_{ijk}^0 v_i v_j v_k + \sum (g_{ij} + \sum g_{ij}^{(k)} v_k) l_i l_j . \quad (2)$$

$G_0(v)$ represents the vibrational energy measured from the ground vibrational state, ω_i^0 are the harmonic fundamental frequencies, x_{ij}^0, y_{ijk}^0, and g_{ij} are the anharmonity parameters, and v_i and l_i are the vibrational and angular momentun quantum numbers. Due to the precision of our data we found it necessary to include a term $g_{ij}^{(k)}$ which represents the vibrational dependence of g_{ij}. Since we used the rotational term scheme $B_{\text{eff}} J(J+1)$ rather than $B_{\text{eff}}(J(J+1) - l^2)$, the l dependent term in Eq. (2) includes the $-B_{\text{eff}} l^2$ term. From the present data (ν_3 fundamental and the two ν_7 hot bands) the anharmonicity parameters $x_{37}^0 + y_{337}^0$, y_{377}^0 and $g_{77}^{(3)}$ could be determined and their values are summarized in Table 5.

In addition it has been possible to obtain the vibrational variation of both the rotational constant $\alpha_3 = B'' - B'$ and the centrifugal distortion constant $\beta_3 = D' - D''$, together with the l-type doubling constant $q_7^{(3)} = q_7' - q_7''$ due to the ν_3 excitation. These constants are also given in Table 5.

Table 5. Derived molecular parameters of HCCCN.

$\omega_3^0 + x_{33}^0 + y_{333}^0$	2079.30606 (71)[a]	cm^{-1}
$x_{37}^0 + y_{337}^0$	− 2.3646 (16)	cm^{-1}
y_{377}^0	0.0032 (12)	cm^{-1}
$g_{77}^{(3)}$	− 0.00416 (38)	cm^{-1}
α_3	13.95 (4)	MHz
β_3	−30.0 (13)	Hz
$q_7^{(3)}$	− 0.072 (42)	MHz

[a] Numbers in parenthesis are one standard deviations.

Conclusion

The present investigation of the ν_3 vibrational band of HC_3N represents the highest resolution study of this molecule to date. The width of the observed lines was essentially limited by the Doppler effect with only a minor amount of pressure broadening. These investigations of HC_3N are the first in a series of experiments to measure and analyse the spectra of carbon chain molecules because their spectra are interesting both from purely spectroscopic and from astrophysical reasons.

The ν_3 vibrational band ($\nu_0 = 2079\ cm^{-1}$) and the two hot bands $\nu_3 + \nu_7 - \nu_7$ and $\nu_3 + 2\nu_7 - 2\nu_7$ have been analysed and it is for the first time that the l-type doubling in the hot bands could be fully

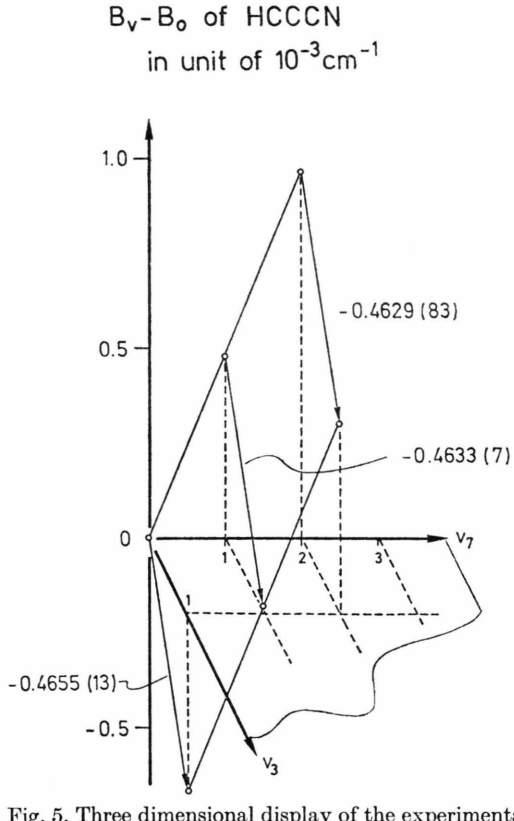

Fig. 5. Three dimensional display of the experimentally determined change of the difference of the rotational constant $B_v - B_0$ in dependence of the vibrational excitation v_3 and v_7. $B_v - B_0$ change linearly with higher excitation in v_7 for $v_3 = 0$ and 1.

resolved. The data were precise enough to derive the dependence of the rotational constants on different vibrational states. Figure 5 summarizes these results in a three dimensional plot of the experimentally determined change of the difference of the rotational constant $B_v - B_0$ in dependence of the vibrational excitation v_3 and v_7. The dependence is shown to be linear to a high degree of accuracy.

Acknowledgement

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