Diode Laser Spectrum of HCCCN near 5 μm

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The ν_3 vibration-rotation band of cyanoacetylene, HC_3N, has been measured in the wavenumber range 2068 to 2095 cm^{-1} to an accuracy of better than ± 0.005 cm^{-1} using a diode laser spectrometer. The width of the observed lines is essentially limited by Doppler-broadening. The band center of the ν_3 vibration is determined from the observed P- and R-branch transitions to be at 2079.30500 (58) cm^{-1}. The rotational constant of the excited state is $B' = 0.151212(10)$ cm^{-1}.

Recently it has become possible to synthesize the long carbon chain molecules HC_3N, HC_5N and HC_7N in the laboratory using both chemical and rf-discharge techniques and to measure their microwave spectra [1–5]. These measurements permitted the rapid detection of the cyanopolyynes in the interstellar medium using radiotelescopes. The molecule cyano-octatetrayne, HC_9N, has also been identified in interstellar space on the basis of theoretical predictions and two observed rotational transitions, although the molecule has not yet been produced in the laboratory [6]. Clearly these molecules must exhibit infrared spectra due to rovibrational transitions and it is important for both theoretical and astrophysical reasons to know precisely where the bands lie and their rotational structure. In this context it is of importance to note that the first infrared spectra of several molecules (i.e. HCCH...) have been detected in the circumstellar/interstellar medium [7]. We have hence begun a program to measure the spectra of carbon chain molecules at high resolution employing tunable diode lasers.

With increasing length of the carbon chain of the cyanopolyyne molecules HC_3N, HC_5N, ... the rotational constant for each species decreases, and thus the spacing of the rotational structure of the vibrational bands decreases as well.

On the other hand the band centers of the C≡C stretching fundamental are expected to suffer only small wavelength shifts and thus this series of molecules is well suited for testing the high resolution capabilities of any infrared spectrometer. In the present study we have chosen cyanoacetylene (cyano-ethyne), HC_3N, as the first target of investigation for a variety of reasons: first the rotational structure of a vibrational band can easily be resolved without suffering from too much confusion by other bands (hot bands); secondly the cyano-acetylene sample can be handled with relative ease; and thirdly the molecular constants of HC_3N are well known, and thus help in securing the assignment. Furthermore in interstellar space HC_3N is, next to HCN, the most widely distributed molecule of the cyanopolyynes and offers in addition the advantage of relatively high column densities in some astronomical sources [8]. Thus it is expected to be detected in space by IR spectroscopy once the observing techniques become available.

The first laboratory measurements of the infrared spectrum of HC_3N were reported in 1957 by Turrell et al. [9] at low resolution. Recently Mallinson and Fayt [10] have remeasured the spectrum using a grating spectrometer in the wavenumber region 1800–6500 cm^{-1}, with a limit of resolution of 0.025 cm^{-1} to 0.05 cm^{-1}. In this paper we report on measurements of the ν_3 rotation-vibration band of HC_3N in the region 2068 to 2095 cm^{-1}, using a diode laser spectrometer*. The width of the observed lines was not determined by the spectrometer, but rather by Doppler effect and a small amount of pressure broadening. Our data hence constitute the highest resolution infrared measurements made on this molecule to date. Apart from

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* The diode laser spectrometer — Model LS-3 — was fabricated by Laser Analytics, Inc., whereas the measurements were carried out at the Universität zu Köln.

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demonstrating the validity of the diode laser technique they permit an improved determination of certain molecular constants.

Although we will report on the new spectrometer elsewhere, we briefly mention the essential features of the present arrangement. Radiation from the diode laser central unit was passed through a 1.5 m long glass-tube sample-cell sealed with BaF_2 windows. The light beam was then directed by a plane-mirror system on to the entrance slit of the monochromator, used for selecting the desired mode of the laser emission. The light emerging from the spectrometer was focussed on a HgCdTe detector cooled with liquid nitrogen. The very precisely known positions of the vibration-rotation lines of CO measured by Guelachvili [11] were used as a calibration standard. The Fabry-Perot fringes of a germanium etalon with a free spectral range of 0.05 cm^{-1} were used as an interpolation scale. The absorption lines were displayed by modulating the laser output frequency with 5 kHz sinewave while slowly sweeping the mean laser frequency through the region of interest. By synchronous demodulation of the detector output signal at 10 kHz the second derivative of the absorption feature was obtained. This source modulation technique is common practise in microwave spectroscopy but not so familiar in conventional infrared spectroscopy.

The cyanoacetylene sample was produced at the Molecular Spectroscopy Laboratory at the Justus-Liebig-Universität, Gießen, by a radiofrequency discharge through a mixture of acetylene and hydrogen cyanide, as discussed by Creswell et al. [1] and Winnewisser et al. [5].

In Fig. 1 we reproduce a part of the HC_3N spectrum recorded with the diode laser system. For purposes of illustration one CO calibration line is included. The strongest transitions of the HC_3N spectrum are assigned to the $\Sigma-\Sigma$ fundamental band, $v_3 = 1 \leftarrow 0$. The narrowly spaced doublets are assigned to the hot band $v_3 = 1$, $v_7 = 1 \leftarrow v_3 = 0$, $v_7 = 1$. The details of this rotational assignment will not be discussed here.

We will now turn to the analysis of the rotational structure of the fundamental band $v_3 = 1 \leftarrow 0$, which consists of a P- and R-branch. The line position ν_m for a P- or R-branch transition is represented by the approximate formula (neglecting centrifugal distortion):

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

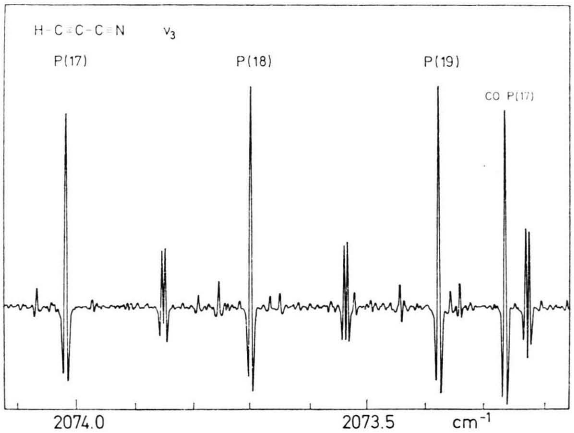

Fig. 1. High resolution diode laser spectrum of the ν_3 vibration-rotation spectrum of HC_3N. Three successive J lines of the P branch are displayed. The P(17) CO line (CO appears as an impurity in the sample) is used as a calibration standard in this section of the spectrum. The weaker doublet lines in the spectrum are hot band transitions and exhibit l-type splitting. The spectrum was recorded by using frequency modulation and is displayed in second derivative form. It may be noted that reflection of laser power back into the laser causes weak energy modulation which produces errors in the baseline.

where $m = J + 1$ for $R(J)$ and $m = -J$ for $P(J)$, and B' and B'' are the rotational constants for the upper and lower state respectively.

In diode laser spectroscopy it is often not possible to cover the range of the band origin which is the case here. Therefore, the rotational assignment cannot be extracted from the present infrared data alone. We have, therefore, used a modified method of combination relations. The parameters ν_0, B', and B'' were derived for hypothetical rotational assignments from the existing body of highly precise line measurements with the help of a least squares method. If one of the three parameters is known from independent measurements to sufficiently high accuracy, the assignment can be secured by the consistency in the values of that parameter. This parameter is generally B'' which is derived from microwave data as is the case here.

In short we used the following procedure: assume that the rotation-vibration lines ν_m are consistently miss-assigned by a constant integral number n to say $p = m + n$. It follows then that (1) can be rewritten by

$$\nu_m = \nu_n + (B_n' + B_n'')\,p + (B_n' - B_n'')\,p^2\,, \quad (2)$$

where

$$\nu_n = \nu_0 - (B' + B'')n + (B' - B'')n^2, \quad (3)$$

$$B_n' + B_n'' = (B' + B'') - 2(B' - B'')n, \quad (4)$$

and

$$B_n' - B_n'' = B' - B''. \quad (5)$$

The parameters ν_n, B_n' and B_n'' are obtained by least squares fit. From (4) and (5) the values of B_n'' are related to the true parameters

$$B_n'' = B'' - n(B' - B''). \quad (6)$$

Therefore the integral number n is given by

$$n = (B'' - B_n'')/(B' - B'') = (B'' - B_n'')/(B_n' - B_n''). \quad (7)$$

Using the last equation the value for B'' as determined by microwave spectroscopy n can be predicted rather accurately. In fact, by this method it became possible to obtain the final assignment in one single iteration.

In Table I the observed wavenumbers are listed together with the final assignment. For comparison we have also listed the calculated wavenumber based on the best fit parameters presented in Table II. The accuracy of the measurements is believed to be better than ±0.005 cm^{-1} on the basis of measurements of the difference between two sets of ^{12}CO and ^{13}CO lines, the latter ones in natural abundance [i.e. ^{12}CO P(16) and ^{13}CO P(5); ^{12}CO P(17) and ^{13}CO P(6)]. At present the accuracy is limited by the thermal instability of the optical path-length of the Ge-etalon. Our results are consistent with those of Mallinson and Fayt [10]. The small discrepancies between the ground state rotational constant B'' quoted in this work and Ref. [1] is caused by contributions from centrifugal distortion neglected in the present work.

Table I. Observed and Calculated Transition Wavenumbers in ν_3 Fundamental Band of HCCCN (cm^{-1}).

J'	J''	Obs.	Calc.	(O−C) × 10^4	J'	J''	Obs.	Calc.	(O−C) × 10^4
56	55	2094.8099	2094.8131	−32	10	9	2082.2894	2082.2875	19
55	54	2094.5600	2094.5617	−17	9	8	2081.9948	2081.9934	14
54	53	2094.3080	2094.3093	−13	8	7	2081.6997	2081.6984	13
53	52	2094.0565	2094.0560	5	7	6	2081.3992	2081.4025	−33
52	51	2093.8043	2093.8018	25					
51	50	2093.5478	2093.5467	11	3	4	2078.0909	2078.0860	49
50	49	2093.2936	2093.2906	30	4	5	2077.7803	2077.7790	13
49	48	2093.0357	2093.0336	21	5	6	2077.4705	2077.4710	− 5
48	47	2092.7784	2092.7757	27	6	7	2077.1604	2077.1621	−17
47	46	2092.5181	2092.5168	13	7	8	2076.8497	2076.8522	−25
46	45	2092.2580	2092.2570	10	16	17	2074.0222	2074.0220	2
45	44	2091.9960	2091.9963	− 3	17	18	2073.7038	2073.7029	9
44	43	2091.7333	2091.7347	−14	18	19	2073.3821	2073.3828	− 7
43	42	2091.4701	2091.4721	−20	19	20	2073.0613	2073.0619	− 6
42	41	2091.2069	2091.2086	−17	20	21	2072.7384	2072.7400	−16
41	40	2090.9437	2090.9442	− 5	21	22	2072.4152	2072.4172	−20
40	39	2090.6784	2090.6789	− 5	29	30	2069.8049	2069.8013	36
39	38	2090.4118	2090.4126	− 8	30	31	2069.4716	2069.4701	15
38	37	2090.1447	2090.1454	− 7	31	32	2069.1372	2069.1380	− 8
37	36	2089.8755	2089.8773	−18	32	33	2068.8033	2068.8050	−17

Table II. Spectroscopic Parameters for ν_3 Fundamental Band of HCCCN in cm^{-1}.

	Present Work	Mallison + Fayt [a]	Creswell et al. [b]
ν_0	2079.30500(58) [c]	2079.306(1)	
$B' + B''$	0.302887(18)		
$B' - B''$	−0.00046350(54)	−0.00046396(60)	
B'	0.151212(10)		
B''	0.151675(10)		0.151740204(13)

[a] From the infrared spectra (10). They also determined $D' - D''$ to be $-0.7(8) \times 10^{-10}$ cm^{-1}.

[b] From the microwave spectra of the ground vibrational state (1). They also determined D'' to be $1.8116(15) \times 10^{-8}$ cm^{-1}.

[c] Numbers in Parantheses represent one standard deviation in the last digit quated.

The analysis of the hot bands arising from successive excitation of ν_7 is in progress, and we will be able to derive new spectral information, such as the l-type doubling constant in the combination state ($v_3 = 1$, $v_7 = 1$), because the l-type splitting is clearly resolved as shown in Figure 1. The present measurements are being extended to isotopically substituted molecules and other cyanopolyynes.

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[1] R. A. Creswell, G. Winnewisser, and M. C. L. Gerry, J. Mol. Spectrosc. **65**, 420 (1977).
[2] P. D. Mallinson and R. L. de Zafra, Mol. Phys. **36**, 827 (1978).
[3] A. J. Alexander, H. W. Kroto, and D. R. M. Walton, J. Mol. Spectrosc. **62**, 175 (1976).
[4] C. Kirby, H. W. Kroto, and D. R. M. Walton, to be published.
[5] G. Winnewisser, R. A. Creswell, and M. Winnewisser, Z. Naturforsch. **33a**, 1169 (1978).
[6] H. W. Kroto, C. Kirby, D. R. M. Walton, L. W. Avery, N. W. Broton, J. M. MacLeod, and T. Oka, Astrophys. J. **219**, L133 (1978).
[7] See for example K. M. Merrill and S. T. Ridgway, Ann. Rev. Astron. Astrophys. **17**, 9 (1979).
[8] G. Winnewisser and C. M. Walmsley, Astrophys. and Space Science **65**, 83 (1979).
[9] G. C. Turrell, W. D. Jones, and A. G. Maki, J. Chem. Phys. **26**, 1544 (1957).
[10] P. D. Mallinson and A. Fayt, Mol. Phys. **32**, 473 (1976).
[11] G. Guelachvili, J. Mol. Spectrosc. **75**, 251 (1979).