Detection of the Infrared Spectrum of Cyanobutadiyne, HC_5N

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The CN stretching band, ν_2, of cyanobutadiyne has been detected by a tunable diode laser spectrometer in the wavenumber range from 2250 to 2260 cm^{-1}. The P- and R-branch transitions, up to P(77) and R(75), of the fundamental band were identified and measured with the accuracy of 0.001 cm^{-1}. The band origin was obtained to be 2256.12406(13) cm^{-1}. The rotational and centrifugal distortion constants in the excited vibrational state, B′ and D′, were also determined.

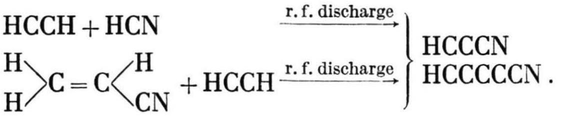
Introduction

Although cyanodiacetylene or cyanobutadiyne, HCCCCCN, is well characterized by its microwave and millimeter wave spectra, its investigation in the infrared region has resisted all attempts so far. The absence of any known low or high resolution IR-spectra of HC_5N may in part be connected with the relative complexity of the synthesis of the molecule resulting in the difficulty of preparing the quantities needed for conventional IR-investigations. On the other hand the large moment of inertia, or the small rotational constant of HC_5N causes a narrowly spaced rotational structure of the vibrational bands which can only be resolved with high spectral resolution. In the present paper we report the detection of the infrared spectrum of HC_5N in the 4.5 μ region recorded with the high spectral resolution provided by tunable diode laser spectroscopy. The width of the observed lines is essentially due to combined Doppler- and pressure broadening whereby the latter contribution is small. At least Doppler-resolution is needed to reveal in this type of spectrum the finer details caused by rotation-vibration interaction.

A program has been started in our laboratory to investigate in the infrared region molecules of astrophysical interest, i. e. those which have already been detected in molecular clouds using radio and infrared techniques and others thought susceptible of being present in space. From this point of view the study of the cyanopolyynes $HC_nN\,(n = 3, 5, \ldots)$ at high resolution in the IR region is particularly rewarding, since their high resolution IR spectra are practically unknown. The aim of this research is thus twofold: to obtain and provide highly precise basic spectral data relevant (i) to the discussion of vibration-rotation theory and (ii) to the interpretation of astrophysical processes possibly associated with rovibrational transitions such as radiative line pumping mechanisms. In the course of this program we have discussed some aspects of the HC_3N spectra in the 5 μ wavelength region of the stretching-vibration of the $C \equiv C$ triple bond [1, 2]. In the present paper we report an analysis of the $C \equiv N$ stretching fundamental ν_2 of the HC_5N. Although a large number of hot bands have been observed and measured, they will be discussed elsewhere.

Experimental

Cyanobutadiyne, HC_5N, was first synthesized by Alexander, Kroto, and Walton [3] in 1975. The HC_5N sample which has been used in the present analysis has been produced by burning a radiofrequency discharge in a mixture of acetylene, HCCH, and hydrogen cyanide, HCN, or acetylene and acrylonitrile, H_2C_2HCN. Both mixtures yielded HC_3N and HC_5N according to



Details of the method were given previously [4]. Aside from the parent molecules the discharge products contained HC_3N and HC_5N which were carefully separated by low temperature distillation, monitored by means of our microwave spectrometer at the Molecular Spectroscopy Laboratory at the Justus Liebig Universität, Giessen. HC_5N is produced in considerably lower quantities than HC_3N.

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However, sufficient HC_5N sample was obtained for performing IR studies. A 60 cm sample cell (sealed by NaCl windows) was used for the present investigation and at pressures ~1 Torr weak absorption lines could be detected.

The infrared spectrum of HC_5N was recorded between 2250 cm^{-1} and 2260 cm^{-1} employing our tunable diode laser spectrometer described by Yamada and Winnewisser [2]. Since our earlier work on HC_3N [1, 2] the operation of the spectrometer has been improved by simultaneous recording of the signal and etalon beams. To achieve single mode operations the 5 kHz modulated laser light was selected by a grating spectrometer and then divided by a germanium beam splitter. The signal beam was directed through the sample cell and the other beam through a 7.5 cm Ge-etalon. Both beams were focused onto two independent Hg-Cd-Te detectors operating at 77 K. Synchronous demodulation of the detector outputs at $2f = 10$ kHz by two independent lock-in amplifiers presents both the spectrum and the etalon fringes in second derivative form.

For calibration purposes a reference cell was placed in the sample beam. Absolute wavenumber standards were achieved in this work by using NNO gas whose rovibrational transitions were measured precisely by Amiot and Guelachvili [5] employing a Fourier transform spectrometer.

In the present work the precision of the measured wavenumbers was about 0.001 cm^{-1}, and was achieved by thermal isolation of the Ge-etalon and calibration of the free spectral range of the etalon for every single scan.

Results

The band of the C ≡ N stretching fundamental ν_2 appears for all cyanopolyyne molecules in the 4.5 μ region and is accompanied by rather strong hot bands. For HC_5N this effect is much more prominent than for HC_3N. Due to the large moment of inertia of HC_5N its rotational structure is considerably more compressed than in the spectra of HC_3N. In addition the very low lying bending-vibrations lead to rather strong hot bands. Superposition of both contributions leads to serious crowding of the spectral lines.

Recently Hutchinson et al. [6] have analysed in the microwave region the bending vibrations ν_{10} and ν_{11} which are considerably lower in energy than all other fundamental vibrations ($\nu_{10} \sim 190$ cm^{-1} and $\nu_{11} \sim 75$ cm^{-1}).

In Fig. 1 a portion of the recorded HC_5N spectrum is presented. It shows the high frequency end of the band. There the equally spaced rovibrational transitions of the ν_2 fundamental constitute the most

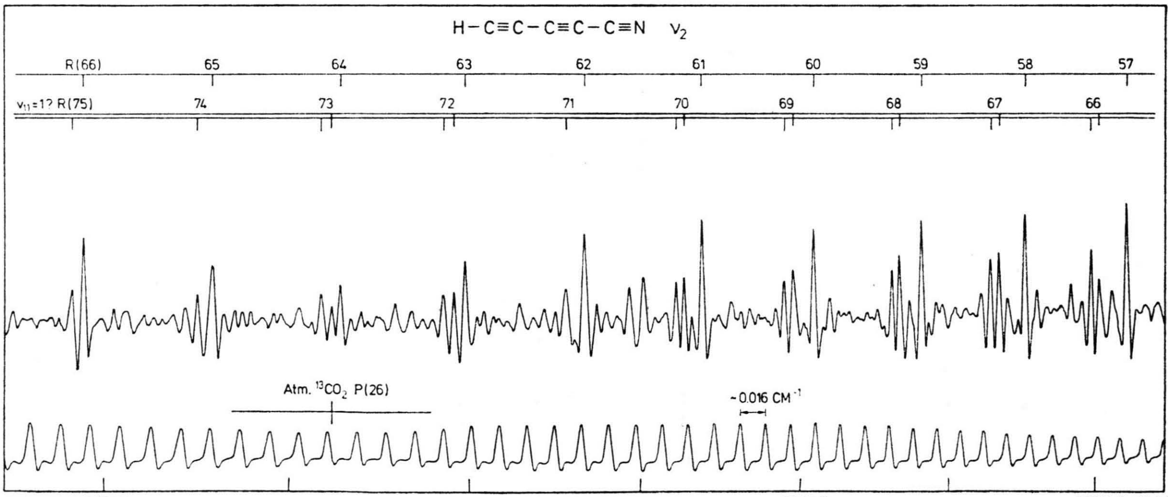

Fig. 1. Portions of the diode laser spectrum of HC_5N near the high frequency end of the band. The spectrum is displayed in second derivative form by 5 kHz frequency modulation of the source and detection at $2f$. The etalon fringes at the lower trace are also in second derivative form. The R(64) and neighbouring lines look weaker than the rest of the spectrum. Atmospheric $^{13}CO_2$ absorbs laser power in that wavenumber region.

prominent feature of the spectrum. Rotational assignments were obtained by an iterative procedure as discussed for HC_3N by Yamada et al. [1]. The almost equally strong set of doublet lines seems to arise from the $v_{11} = 1$ series. They will not be discussed in this paper.

Near the band origin (2256 cm^{-1}), the spectrum is considerably more complicated as shown in Figure 2. Although the spectrum was recorded at -20 °C, many overlapping hot bands lead to serious confusion of that part of the spectrum. Whereas the assignments of the rovibrational transitions of the fundamental band are unambiguous, the $v_{11} = 1$ rotational assignments have to be considered tentative at present. By cooling the gas in the cell to -20 °C the width of lines was reduced compared to those recorded at room temperature. However, the cooling was not sufficient to enhance the intensity of the lines of the fundamental position. Thus their assignment rests on calculated values based on the uniquely assigned higher transitions. The experiment will be repeated at lower temperatures.

The observed rovibrational transitions of the ν_2 fundamental are listed in Table 1 and the spectroscopic parameters derived from a least squares fit to the measured data are summarized in Table 2.

The identification and analysis of the ν_2 fundamental band rest heavily on the available microwave and millimeter wave data [7]. The rotational numbering was confirmed by the agreement between the ground state rotational constants derived from the infrared spectrum and those derived from the microwave-millimeter wave data. This procedure is analogous to the one we used in our earlier work on HC_3N [2]. By using only the infrared data a value for $B'' = 1331.395(53)$ MHz was obtained, which is in agreement within two standard deviation to the most recent value of $B'' = 1331.33271$ MHz obtained from a combined analysis of microwave and millimeter wave data [7]. In the final least squares fit, the ground state parameters B'' and D'' were kept fixed at the microwave values. The 120 measured lines of the ν_2 fundamental were fitted with a standard deviation of 0.0007 cm^{-1}. The derived band origin at 2256.124 cm^{-1} is slightly lower than that of HC_3N which is located at 2273.996 cm^{-1} [8].

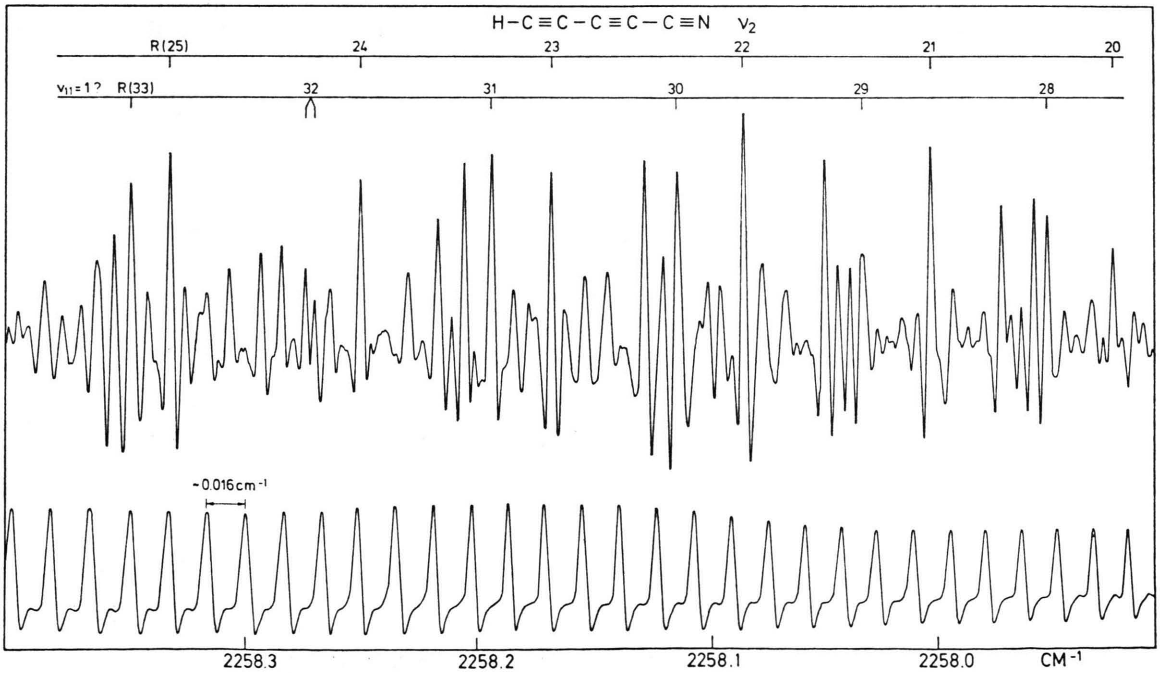

Fig. 2. High resolution diode laser spectrum near the ν_2 band origin of HC_5N. The identification of the hot bands is tentative.

Table 1. Transition wavenumbers of the ν_2 fundamental band of HC_5N in cm^{-1}.

$J' - J''$	calc.	obs.-calc.	$J' - J''$	calc.	obs.-calc.
76 − 77	2248.4381	0.0011	1 − 0	2256.2126	− 0.0013
75 − 76	2248.5488	0.0005	2 − 1	2256.3008	− 0.0016
74 − 75	2248.6593	0.0007	4 − 3	2256.4764	0.0007
73 − 74	2248.7694	− 0.0004	5 − 4	2256.5638	0.0003
72 − 73	2248.8793	− 0.0003	6 − 5	2256.6508	0.0005
71 − 72	2248.9888	0.0000	19 − 18	2257.7562	0.0001
70 − 71	2249.0981	0.0028	20 − 19	2257.8392	− 0.0004
69 − 70	2249.2071	− 0.0009	21 − 20	2257.9219	0.0004
56 − 57	2250.5984	0.0001	22 − 21	2258.0043	− 0.0008
55 − 56	2250.7034	0.0000	23 − 22	2258.0864	− 0.0002
54 − 55	2250.8081	0.0006	24 − 23	2258.1683	0.0006
53 − 54	2250.9126	0.0013[a]	25 − 24	2258.2498	0.0010
52 − 53	2251.0167	0.0004[a]	26 − 25	2258.3310	0.0002
51 − 52	2251.1206	0.0004[a]	27 − 26	2258.4120	0.0002
50 − 51	2251.2242	0.0003[a]	28 − 27	2258.4927	0.0009
49 − 50	2251.3275	0.0004[a]	29 − 28	2258.5730	0.0008
48 − 49	2251.4305	− 0.0002[a]	30 − 29	2258.6531	0.0004
47 − 48	2251.5332	0.0010[a]	31 − 30	2258.7329	0.0004
46 − 47	2251.6357	0.0006	32 − 31	2258.8124	0.0007
45 − 46	2251.7378	0.0002	33 − 32	2258.8916	0.0003
44 − 45	2251.8397	0.0005	35 − 34	2259.0491	0.0006
43 − 44	2251.9413	0.0007	36 − 35	2259.1275	0.0006
42 − 43	2252.0425	0.0006	37 − 36	2259.2055	0.0008
41 − 42	2252.1435	0.0004	38 − 37	2259.2833	0.0006
40 − 41	2252.2443	0.0002	41 − 40	2259.5148	0.0007
39 − 40	2252.3447	− 0.0003	42 − 41	2259.5914	0.0003
38 − 39	2252.4448	− 0.0006	43 − 42	2259.6677	− 0.0003
37 − 38	2252.5447	− 0.0002	44 − 43	2259.7437	0.0000
36 − 37	2252.6442	− 0.0001	45 − 44	2259.8194	− 0.0001
35 − 36	2252.7435	− 0.0003	46 − 45	2259.8948	− 0.0001
34 − 35	2252.8425	− 0.0003	47 − 46	2259.9700	− 0.0004
33 − 34	2252.9412	− 0.0007	48 − 47	2260.0448	− 0.0001
32 − 33	2253.0396	− 0.0003	49 − 48	2260.1194	− 0.0002
31 − 32	2253.1377	− 0.0001	50 − 49	2260.1937	− 0.0005
30 − 31	2253.2355	− 0.0009	51 − 50	2260.2677	− 0.0006
29 − 30	2253.3330	− 0.0005	52 − 51	2260.3413	− 0.0006
28 − 29	2253.4303	− 0.0002	53 − 52	2260.4148	− 0.0007
27 − 28	2253.5272	− 0.0004	54 − 53	2260.4879	− 0.0008
26 − 27	2253.6239	− 0.0002	55 − 54	2260.5607	− 0.0003
25 − 26	2253.7203	0.0001	56 − 55	2260.6332	− 0.0002
24 − 25	2253.8164	0.0004	57 − 56	2260.7055	− 0.0008[a]
19 − 20	2254.2924	0.0007	58 − 57	2260.7774	− 0.0008[a]
18 − 19	2254.3868	0.0000	59 − 58	2260.8491	− 0.0005[a]
17 − 18	2254.4808	0.0000	60 − 59	2260.9205	− 0.0005[a]
16 − 17	2254.5746	0.0005	61 − 60	2260.9916	− 0.0010[a]
15 − 16	2254.6681	− 0.0006	62 − 61	2261.0624	− 0.0007[a]
14 − 15	2254.7612	0.0002	63 − 62	2261.1329	− 0.0001[a]
13 − 14	2254.8541	0.0001	64 − 63	2261.2032	− 0.0001
12 − 13	2254.9467	− 0.0002	65 − 64	2261.2731	− 0.0005
11 − 12	2255.0390	− 0.0003	66 − 65	2261.3428	0.0011
10 − 11	2255.1311	0.0000	67 − 66	2261.4121	0.0004
9 − 10	2255.2228	− 0.0008	68 − 67	2261.4812	0.0001
8 − 9	2255.3142	− 0.0005	69 − 68	2261.5500	− 0.0005
7 − 8	2255.4054	− 0.0010	70 − 69	2261.6185	0.0001
6 − 7	2255.4962	− 0.0007	71 − 70	2261.6867	− 0.0018
5 − 6	2255.5868	− 0.0005	72 − 71	2261.7547	− 0.0005
4 − 5	2255.6771	− 0.0004	73 − 72	2261.8223	− 0.0014
3 − 4	2255.7670	0.0013	74 − 73	2261.8897	− 0.0002
2 − 3	2255.8567	0.0004	75 − 74	2261.9567	0.0014
1 − 2	2255.9461	− 0.0002	76 − 75	2262.0235	0.0009

[a] The lines measured twice independently. The average wavenumbers with double weight were used in the fit.

Table 2. Spectroscopic Parameters of HCCCCCN in the ν_2 Fundamental Band[a].

ν_0	2256.12406 (13)	cm^{-1}
B'	1326.9663 (36)	MHz
B''	1331.33271 (fixed)	MHz[b]
D'	27.05 (66)	Hz
D''	30.10 (fixed)	Hz[b]

[a] The numbers in the parentheses are one standard deviation in the unit of the last digit.

[b] Fixed at the value of [7].

Conclusion

The present investigation of the ν_2 fundamental band of HC_5N represents the first study of this molecule in the infrared region. This investigation was undertaken within the framework of extensive laboratory studies of the cyanopolyyne series. These high resolution IR investigations will be extended to the bending vibrations. Judging from the density of the lines in the spectrum of HC_5N, it is believed that the IR spectra of HC_7N can also be studied by diode laser spectroscopy, provided contributions from a large number of the expected hot bands can be suppressed by proper cooling of the molecule. Since a large number of cyanopolyyne molecules have been detected in space [9 – 12] by radio astronomy one can expect that this class of molecules represent likely candidates to be detected in future by infrared technique. The present high resolution IR spectra are assumed to be an aid for future astronomical searches.

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