The v_5 and v_6 Fundamental Bands of HCCCN[1]

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The bending fundamental bands of HCCCN, v_5 and v_6, have been recorded in the region from 470 to 700 cm^{-1} with a resolution of 0.04 cm^{-1} using an FT spectrometer. The band centers have been determined precisely; $v_5 = 663.2220(10)$ and $v_6 = 498.8022(10)$ cm^{-1}. From the obtained effective rotational constants, the sign of the *l*-type doubling constants has been determined to be positive for the $v_5 = 1$ and $v_6 = 1$ vibrational states.

To our surprise no high resolution infrared study has been reported for the three bending fundamentals of cyanoacetylene, HCCCN. The spectra of these bands had been measured with low resolution by Turrell et al. [1] and Job and King [2]. The band origins were roughly determined by them to be $v_5 = 663$, $v_6 = 500$, and $v_7 = 230$ cm^{-1}. The last number was obtained from the Raman spectrum in liquid phase [2]. On the other hand the rotational spectra of this molecule have been studied very extensively for the ground vibrational states [3], and for several excited vibrational states [4, 5, 6]. The rotational constants of this molecule in these low energy excited states have been determined very precisely. However, the vibrational energy and the sign of the *l*-type doubling constants can not be obtained from the pure rotational spectra. The present study was thus carried out in order to determine those for the v_5 and v_6 fundamental bending states.

The spectra were obtained by a Nicolet Series 8000 vacuum spectrometer equipped with a 3 μm Mylar beam splitter and a Cu:Ge detector, using a cell of 18.7 cm path length and a gas pressure of about 600 Pa. The measurement was carried out at room temperature. The spectra were calibrated with N_2O lines [7]. The resolution was about 0.04 cm^{-1}, and the absolute wavenumber accuracy of the line positions measured with a peak-finder routine is 0.001 cm^{-1} for unblended lines. The sample of HCCCN was prepared from HCCCHNOH and P_4O_{10}.

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The observed spectra of the v_5 and v_6 fundamental bands exhibit typical $\Pi - \Sigma$ band structure with an intense *Q* branch at the center and relatively weak P and R branches. Figures 1 and 2 show the v_5 and v_6 band observed in the present work. For both fundamental bands, the *Q* branch shows a band head structure at the low frequency side formed by the unresolved low-*J* components. We have analyzed 145 P and R branch transitions from P (80) to R (75) for the v_5 band and 105 transitions from P (58) to R (57) for the v_6 band. The measured transition wavenumbers of these P and R branch transitions were analyzed by least squares fits using the following empirical expression:

$$\nu(J' - J'') = \nu_0 + B'J'(J'+1) - D'[J'(J'+1)]^2 - B''J''(J''+1) + D''[J''(J''+1)]^2, \quad (1)$$

where ν_0 is the band center, *B*'s are the effective rotational constants, and *D*'s are the centrifugal distortion constants. The lower vibrational state was the ground state for the present cases. The constants for the ground state, B'' and D'', were fixed at the values obtained by microwave spectroscopy [3], and the three parameters, ν_0, B', and D', were determined by a least squares analysis. Since the vibrational angular momentum is not zero in both $v_5 = 1$ and $v_6 = 1$ states, i.e. $l = 1$, the parameters for the upper state in Eq. (1) include effectively the *l*-dependent contributions as well as the *l*-type doubling contributions.

The obtained standard deviation of the fits reflected faithfully the uncertainty of the line position measurements; 0.0015 cm^{-1} for the v_5 band and 0.0016 cm^{-1} for the v_6 band. The obtained constants are listed in Table 1. Higher order corrections for

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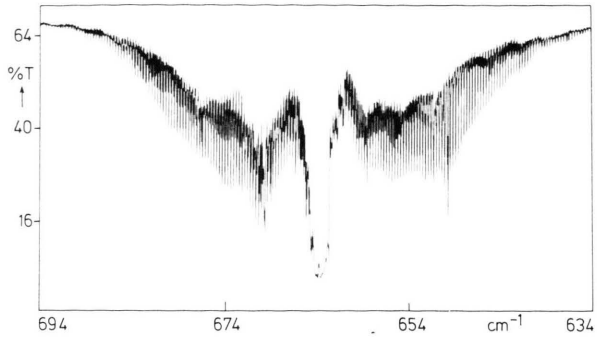

Fig. 1. The ν_5 band observed in the present work.

Table 1. Band parameters obtained from the ν_5 and ν_6 fundamentals [a].

Constant	ν_5 band	ν_6 band	Unit
ν_0	663.22203(26)	498.80223(39)	cm^{-1}
B'	4549.4008(69)	4556.525(18)	MHz
D'	0.5539(12)	0.5439(52)	kHz

[a] The ground state constants were fixed at the values obtained by microwave spectroscopy [3]: $B'' = 4549.0579$ MHz and $D'' = 0.54311$ kHz. The numbers in the parentheses correspond to one standard deviation in the unit of the last digit quoted. Including the calibration error, the uncertainties for the band origins were estimated to be ± 0.001 cm^{-1}.

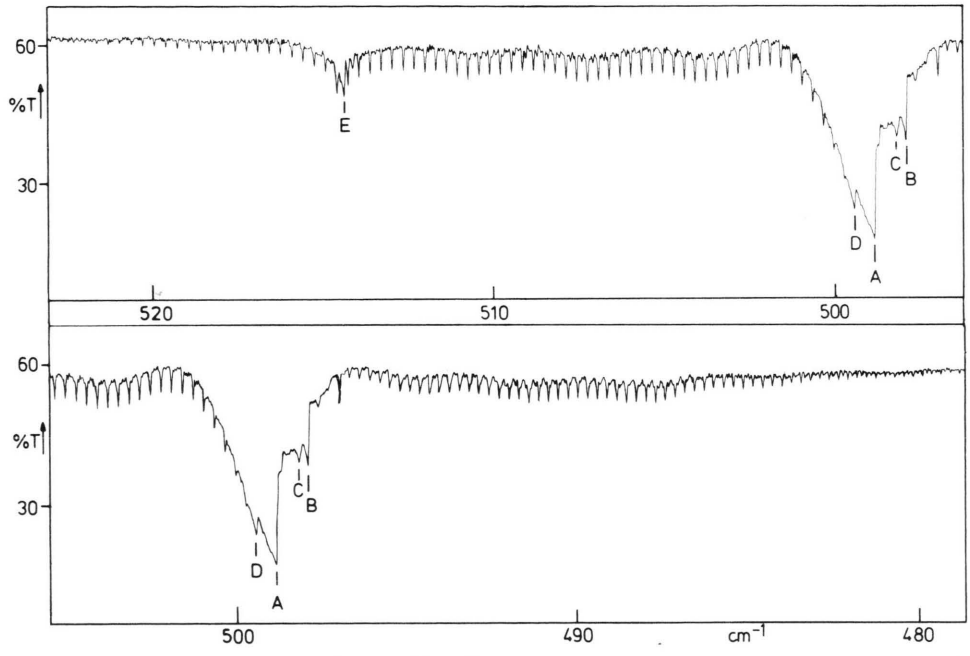

Fig. 2. The observed ν_6 band is shown with indications of the identified Q branches; A is the Q branch of the fundamental band and B, C, D, and E are of hot bands, the assignments of which are given in Table 2.

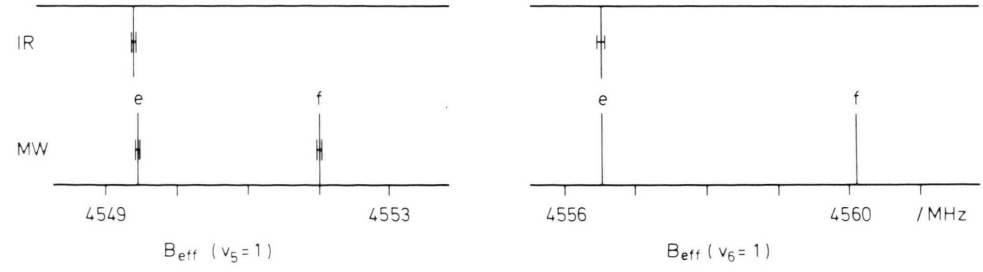

Fig. 3. The obtained effective rotational constants are compared with those determined by microwave spectroscopy [5]. The error bars indicate three times the standard deviation. For the microwave data of the $\nu_6 = 1$ state the error bars are too small to be indicated. The rotational constants obtained from the both ir bands correspond to the values of the lower component of the *l*-type doubling obtained by microwave spectroscopy. This fact leads us to the conclusion that the *l*-type doubling constants are positive for the $\nu_5 = 1$ and $\nu_6 = 1$ state.

Table 2. Positions of Q branches assigned to hot bands associated with the v_6 band[a].

Peak	Wavenumber in cm^{-1}	Assignment
B	497.898	$(1, 1)^{0+} - (0, 1)^1$
C	498.158	$(1, 1)^{0-} - (0, 1)^1$
		$(1, 1)^2 - (1, 0)^1$
D	499.411	$(2, 0)^2 - (1, 0)^1$
E	514.399	$(2, 0)^0 - (1, 0)^1$

[a] Assignments are given by indicating the lower and upper state by $(v_6, v_7)^l$, where $l = l_6 + l_7$. The + and − signs are used to distinguish the vibrational l-doubling components [5].

the centrifugal distortion were found to be ignorable.

The obtained effective B values are compared in Fig. 3 with those from microwave spectra. This figure clearly shows that the P and R transitions of both the v_5 and v_6 fundamental bands, which were analyzed in the present study, connect the ground state with the lower components of the l-type doublets in the excited states. From this fact we have assigned the symmetry of the l-doubling components based on the dipole selection rules; e − e or f − f for the P and R transitions [8]. Thus the symmetry of the lower component of the l-type doublet in the $v_5 = 1$ and $v_6 = 1$ state was determined to be the same as that of the ground vibrational state, which is of symmetry "e". This means that the l-type doubling constants q_5 and q_6 of HCCCN are positive as discussed in Ref. [9, 10, 11].

As discussed by Yamada and Creswell [5] the $v_5 = 1$ state is perturbed by the $v_7 = 3$ state due to a weak anharmonic resonance. The presently obtained centrifugal distortion constant is slightly large for this state, which suggests the presence of such an interaction. Since the precision of the present data was not as high as those obtained by microwave spectroscopy, we could not improve the rotational analysis and interaction analysis of Yamada and Creswell [5] any further by adding the present data.

Several hot and band Q branches associated with the v_6 fundamental band, indicated in Fig. 1 by B, C, D, and E, were identified as listed in Table 2. The Q branch position for the $2\,v_6^0 - v_6^1$ was found far away from the main band center, although the other component, $2\,v_6^2 - v_6^1$ was found in the band center region. This shift is caused by Fermi resonance between the $v_6 = 2$ ($l = 0$) and the $v_4 = 1$ state [5], where v_4 is the lowest stretching fundamental mode; v_4 is 884.766 cm^{-1} [12]. Thus the observed separation between the $l = 2$ and $l = 0$ levels of the $v_6 = 2$ state is extraordinarily large, about 15 cm^{-1}. In the v_5 spectrum we have also observed several absorption peaks which may be Q branches of hot bands. However we could not assign them definitely.

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