Analysis of "Hot" Bands Associating to the ν_2 Fundamental Band of HC_5N [1]

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The ν_2 fundamental band of cyanobutadiyne, HC_5N, is accompanied by a number of strong hot bands arising from the low energy bending exicted states. We have assigned and analyzed the hot band from the $v_{11} = 1$, 2, and 3 states and the $v_{10} = 1$ state. The *l*-type doubling effect has been observed in the hot band of $v_{11} = 1$, while the hot band of $v_{10} = 1$ did not show the splitting. The diode laser spectra were recorded between 2250 and 2260 cm^{-1}.

Introduction

The first high resolution infrared spectrum of HC_5N was recorded by us [1] in 1981 using a tunable diode laser; a low resolution spectrum was measured earlier by Kroto and coworkers [2]. The Doppler limited HC_5N spectra were obtained for the CN-stretching vibration ν_2 in the 2255 cm^{-1} region. The fundamental band is accompanied by a number of intense hot bands arising from the low frequency bending vibrations ν_{11} and ν_{10} ($\nu_{11} \cong 75\,cm^{-1}$ and $\nu_{10} \cong 190\,cm^{-1}$ [3]). In the present paper we report the assignment and analysis of the hot bands arising from the $v_{11} = 1$, 2, and 3 states and the $v_{10} = 1$ state. In the following the vibrational states are labelled as $(v_2; v_{10}, v_{11})^l$, where l is the quantum number for the sum of the vibrational angular momenta associated with the bending vibrations ν_{10} and ν_{11}.

Assignments and Analysis

At the high frequency end of the observed spectrum we found a series of doublet lines (see Fig. 1 of [1]), which were assigned to the $\Pi - \Pi$ hot band arising from the $v_{11} = 1$ state, $(1; 0, 1)^1 - (0; 0, 1)^1$. We extended the assignment in the low frequency direction using a Loomis-Wood diagram [4]. The line position of each l component was first analyzed by the conventional formula

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

where $m = -J''$ for the P branch and $m = J'' + 1$ for the R branch. The correct J number was found by the iteration procedure described in [5]: the B'' constant obtained from the fit using (1) has to agree with the effective B value of the $(0; 0, 1)^1$ state obtained by microwave spectroscopy [3]. This assignment was further confirmed by the consistency in the e-e and f-f components of the doublet.

For the other hot bands, the assignments were not so simple because the observed spectra did not exhibit any characteristic doublet or triplet structure. A part of the observed spectrum is shown in Fig. 1, with the final assignments. For every series of lines found in the Loomis-Wood diagram, we tried the fit using (1) with various possible J assignments. Finally three additional series of lines could be assigned to the hot bands $(1; 0, 2)^2 - (0; 0, 2)^2$, $(1; 0, 3)^3 - (0; 0, 3)^3$, and $(1; 1, 0)^1 - (0; 1, 0)^1$.

The assigned lines were then analyzed by using the expression

$$\nu(J' - J'') = \nu_0 + B'J'(J'+1) - D'J'^2(J'+1)^2 - B''J''(J''+1) + D''J''^2(J''+1)^2 \qquad (2)$$

with the constraint $D' = D'' = 30$ Hz [3]. The agreement between the B'' constants obtained from the ir data and the microwave data is good within 3 times the standard deviation and is schematically shown in Figure 2. The effective parameters are listed in Table 1.

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[2] Two middle initials, M. T., are newly added to the name of Koichi Yamada in order to remove the ambiguity which may arise in this common japanese name.

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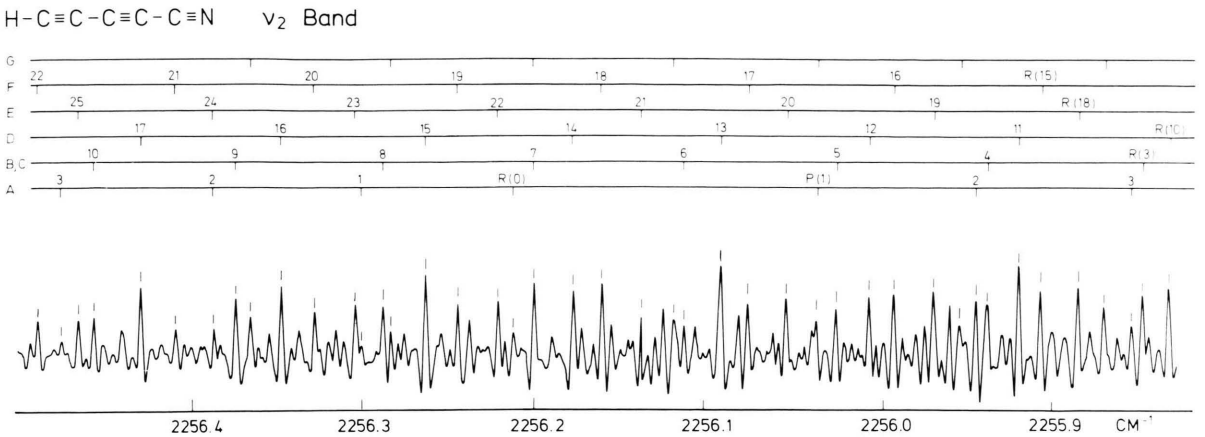

Fig. 1. A part of the observed spectrum showing the region near the band origin of the fundamental ν_2. The assigned bands are indicated as the series A to F; $A = (1; 0, 0)^0 - (0; 0, 0)^0$, B and $C = (1; 0, 1)^1 - (1; 0, 1)^1$, $D = (1; 0, 2)^2 - (1; 0, 2)^2$, $E = (1; 0, 3)^3 - (1; 0, 3)^3$, and $F = (1; 1, 0)^1 - (1; 1, 0)^1$. G forms also a series, but has not yet been identified.

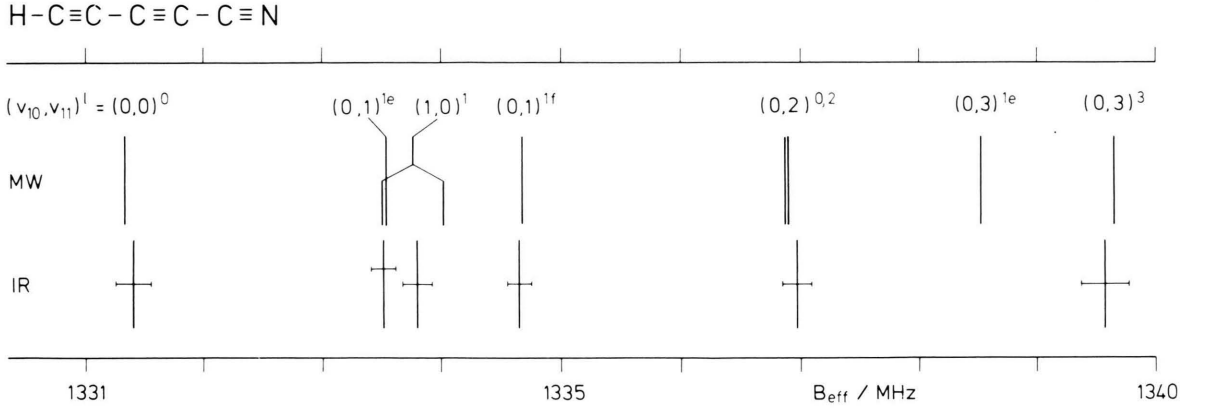

Fig. 2. The effective B values of the lower states obtained from the ir data are compared with those from microwave data [3]. The error bars for the ir data show three times standard deviation. The error in the values for the microwave data is too small to be indicated.

Table 1. Spectroscopic parameters of HC_5N in the hot bands associated to the ν_2 fundamental[a].

Band	ν_0/cm^{-1}	B'/MHz	B''/MHz
$(1; 0, 1)^{1e} - (0; 0, 1)^{1e}$	2255.49800(14)	1329.176(28)	1333.516(28)
$(1; 0, 1)^{1f} - (0; 0, 1)^{1f}$	2255.49779(17)	1330.306(30)	1334.644(30)
$(1; 0, 2)^2 - (0; 0, 2)^2$	2254.87320(14)	1332.697(44)	1336.968(44)
$(1; 0, 3)^3 - (0; 0, 3)^3$	2254.24303(15)	1335.303(63)	1339.582(65)
$(1; 1, 0)^1 - (0; 1, 0)^1$	2254.52393(10)	1329.473(34)	1333.766(35)

[a] The vibrational states are labeled by $(v_2; v_{10}, v_{11})$. The numbers in parentheses are one standard deviations obtained by the least squares fit in the units of the last digit. The effective centrifugal distortion constants are assumed to be $D' = D'' = 30$ Hz [3].

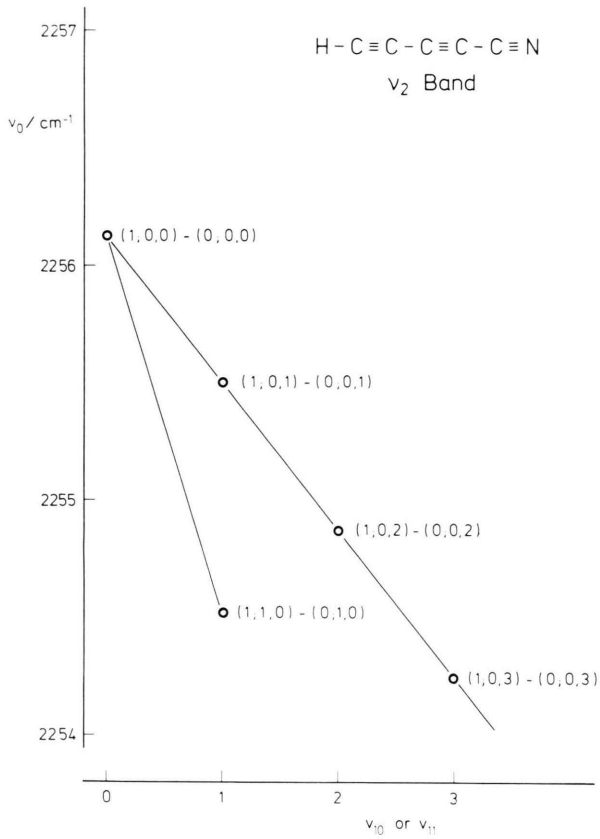

Fig. 3. The obtained band origins are plotted for v_{10} and v_{11} quantum number. A good linear dependence can be seen for v_{11} series.

Summary

A total of 210 lines from P (76) to R (75) arising both from the $(1; 0, 1)^{1e} - (0; 0, 1)^{1e}$ transitions and from the $(1; 0, 1)^{1f} - (0; 0, 1)^{1f}$ transitions were assigned. The l-type doubling constants q_{11} of both the $(1; 0, 1)^1$ and $(0; 0, 1)^1$ state can be calculated from the effective B values listed in Table 1 to be 1.130(45) MHz; they are in agreement with each other to within one standard deviation.

All other measured hot bands did not show any observable effects of l-type interaction. For example none of the 68 lines of the hot band $v_{11} = 2$, covering P (45) to R (45), show an indication of l-type splitting. Since the effective B values for the $l = 0$ and 2 state of the (0; 0, 2) state are very close, as shown in Fig. 2, we can not identify the l quantum number for this hot band. However, we believe that the observed lines arise from $l = 2$, since due to the $l = 2$ degeneracy the lines should be twice as strong as for $l = 0$.

63 lines were assigned to the $(1; 0, 3)^3 - (0; 0, 3)^3$ transitions from P (39) to R (58). In this case the l assignment is unique, as shown in Figure 2. Yet the doublet series for the $l = 1$ state has not been found.

60 lines were assigned to the $(1; 1, 0)^1 - (0; 1, 0)^1$ transitions from P (42) to R (51). The l-doubling effect was not observed. Figure 2 shows that the effective B value for the lower state obtained from the ir data is very close to the average of those of the e and f component obtained from the microwave data.

The band origins thus obtained are graphically shown in Fig. 3, where we can see a linear v dependence of the band origins for the v_{11}, which suggests that the v_{11} vibration is well separated from the v_2 stretching mode. In addition this regular dependence supports strongly the assignments of the v_{11} hot bands made in the present study. The list of the transition wavenumbers used in the analysis can be obatined from the authors upon request.

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