

Infrared Spectrum of $^{15}\text{N}^{13}\text{C}^{13}\text{C}^{15}\text{N}$ near 2100 cm^{-1}

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The high resolution infrared spectrum of the linear centro-symmetric molecule $^{13}\text{C}_2^{15}\text{N}_2$ (cyanogen) has been measured in the region from 1950 to 2150 cm^{-1} . The ν_3 fundamental band and the difference band $\nu_1 - \nu_5$ were observed in that region. Hot-band transitions arising from the ν_5 , $2\nu_5$, $3\nu_5$, and ν_4 levels were also measured with the ν_3 band. The ν_3 fundamental band and first hot band for $^{15}\text{N}^{12}\text{C}^{13}\text{C}^{15}\text{N}$ were also measured. © 1998 Academic Press

INTRODUCTION

During the course of some measurements on a sample of isotopically enriched $\text{H}^{13}\text{C}^{15}\text{N}$ we discovered the spectrum of $^{15}\text{N}^{13}\text{C}^{13}\text{C}^{15}\text{N}$, which was inadvertently produced as a small impurity. To our knowledge this is the first observation of a sample of totally substituted cyanogen. Weak lines were also found for the $^{15}\text{N}^{12}\text{C}^{13}\text{C}^{15}\text{N}$ isotopomer that was present as an even smaller impurity.

Earlier high resolution measurements were made in the 2100-cm^{-1} region on the normal isotopomer of cyanogen ($I-4$) and on the ^{15}N doubly substituted isotopomer (I). Those earlier measurements identified a number of hot-band transitions as well as the ν_3 band that originates in the ground vibrational state. Maki (I) first observed and Picard ($3, 4$) made detailed measurements on the difference band $\nu_1 - \nu_5$, which can also be found in the 2100-cm^{-1} region and which can be used to locate the ν_1 level from infrared measurements if the ν_5 level has been measured. Of course, ν_1 can also be measured using Raman spectra as shown by Jones ($5, 6$) and Wang and Weber (7) as well as by very recent measurements by Bermejo *et al.* (8).

Recent far infrared high resolution measurements have been made by Grecu *et al.* to characterize the lowest vibrational states of the normal isotopomer of cyanogen (9) and a number of other isotopomers (10). More of that work will soon be published.

Cyanogen is a linear molecule belonging to the $D_{\infty h}$ point group. Because of the spin $\frac{1}{2}$ parity of both the ^{15}N and ^{13}C atoms, the transitions of $^{15}\text{N}^{13}\text{C}^{13}\text{C}^{15}\text{N}$ show an intensity alternation that is useful in assigning the transitions. For $g(e)$ states, such as the ground vibrational state, the population ratio $J_{\text{even}}/J_{\text{odd}}$ is $\frac{5}{3}$, aside from any Boltzmann effects. For $g(f)$ states the ratio is $J_{\text{even}}/J_{\text{odd}} = \frac{3}{5}$. For the u states the populations are reversed, $u(e)$ $J_{\text{even}}/J_{\text{odd}} = \frac{3}{5}$ and $u(f)$, $J_{\text{even}}/J_{\text{odd}} = \frac{5}{3}$. Of course, the intensity ratios follow the population ratios. In infrared spectra the ν_3 band is a parallel

band, and it is difficult to be certain of the band center for parallel bands. The observed intensity alternation confirms that we have correctly assigned the J values and vibrational states for these bands.

There is no such intensity alternation for $^{15}\text{N}^{12}\text{C}^{13}\text{C}^{15}\text{N}$, which has $C_{\infty v}$ symmetry. The accuracy of the assignments for that isotopomer rests in part on the constants found for the heavier isotopomer.

EXPERIMENTAL DETAILS

The spectrum was recorded from 1900 to 2350 cm^{-1} on the Bruker IFS120HR interferometer in the Giessen laboratory. The unapodized instrumental resolution was about 0.0028 cm^{-1} . A white-type multipass glass cell with a base length of 0.82 m and a total optical pathlength of 13.28 m was used. The pressure of gas in the cell was about 1 mbar and consisted primarily of HCN with only a trace of the cyanogen gas.

The sample was prepared by slowly dropping a threefold excess of distilled water into an equimolar mixture of 13 mmol isotopically labelled potassium cyanide ($^{13}\text{C} \approx 99\%$, $^{15}\text{N} \approx 98\%$ purchased from Cambridge Isotope Laboratories, Andover, MA) and phosphorus pentoxide according to the method described by King and Nixon (11). The gas evolved was passed in a nitrogen gas stream through P_2O_5 and condensed in a liquid nitrogen cooled trap. Subsequently, the condensate was purified by vacuum distillation and stored at liquid nitrogen temperature. For transferring the sample into the absorption cell, the storage glass tube was warmed up to approximately 200 K . The occurrence of cyanogen as a byproduct of the described HCN synthesis under mild conditions was unexpected, since NCCN is known from the literature (12) to be formed from HCN only by either catalyzed oxidative cleavage or thermal decomposition at high temperature. The former path would seem to be the most likely at the low temperatures involved in the preparation.

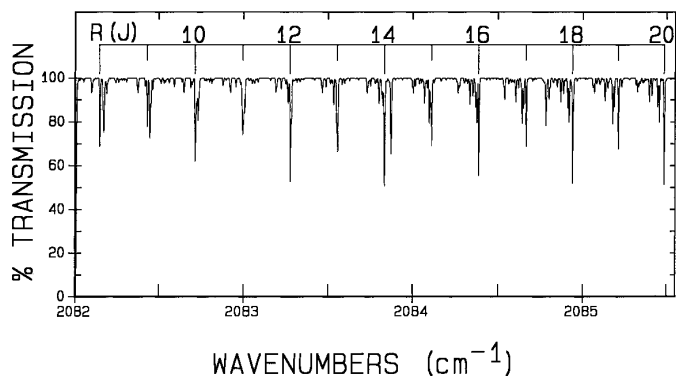


FIG. 1. Spectrum of $^{15}\text{N}^{13}\text{C}^{13}\text{C}^{15}\text{N}$ with the J'' values for the R -branch lines for ν_3 indicated above the spectrum. One can see that the transitions with J'' even are stronger than those for which J'' is odd.

The cyanogen yield turned out to be only minute, and its observed concentration might even have been enriched relative to hydrogen cyanide during the transfer of the sample into the absorption cell due to its 10-fold higher vapor pressure at the low temperature used for the transfer.

The spectrum was calibrated internally by the addition of a small amount of OCS and CO. Calibration data were taken from the NIST World Wide Web listing (13). The uncertainties given in the tables are twice the standard deviation given by the least-squares analysis of the measurements. In addition, one should add in quadrature to the band centers the absolute calibration uncertainty of $\pm 0.0006 \text{ cm}^{-1}$.

ASSIGNMENT AND ANALYSIS OF THE SPECTRUM

The ν_3 Fundamental Band

The strongest band observed in the 2100-cm^{-1} region is the ν_3 band. Along with this band we found a great many hot-band transitions, some of which could not be assigned with confidence even though a clear series of transitions was observed. In this paper we report only the assignments for which we are certain. The strongest band is obviously due to transitions from the ground state, and the other very strong sub-bands must be due to transitions from the lowest vibrational states, ν_5 , $2\nu_5$, and ν_4 . Earlier measurements of the rotational constants for these states for other isotopomers (1–10) provided a good guide to the rotational constants to be expected for $^{13}\text{C}_2^{15}\text{N}_2$. In addition, the intensity alternation expected for the different states was a valuable guide to the correct J assignments. Figure 1 shows a portion of the R -branch region of ν_3 . Although some hot-band lines overlap with the transitions from the ground state, the $\frac{5}{3}$, $J_{\text{even}}/J_{\text{odd}}$, intensity alternation is obvious in Fig. 1. One can also see the barely resolved doublet structure of the first hot-band transitions with their intensity alternations at the high wavenumber part of the figure. While not included in this

paper, we have prepared a set of tables listing all of the observed wavenumbers of the transitions and the deviations from the fit (observed – calculated). These tables are available from the authors as ASCII files that can be sent by e-mail.

Once the hot bands arising from the ν_5 and $2\nu_5$ bands had been analyzed, it was easy to predict and assign the $\nu_3 + 3\nu_5 - 3\nu_5$, $\Pi_g - \Pi_u$, and $\Phi_g - \Phi_u$ transitions. The splitting of the $\Phi - \Phi$ transitions was too small to observe, but the lack of an intensity alternation was evidence that the vibrational assignment is correct.

For those cases where ν_5 and $\nu_4 = 0$ or 1, the measured transitions were fit to the usual equations:

$$E_v = G_v + B_v J(J+1) - D_v [J(J+1) - k^2]^2 \pm \frac{1}{2} \delta_{l,1} [q_v J(J+1) - q_{vj} J^2 (J+1)^2], \quad [1]$$

$$\nu_{\text{obs}} = E'_v - E''_v, \quad [2]$$

and

$$\nu_c = G'_v - G''_v. \quad [3]$$

In Eqs. [1] and [2] B_v and D_v are the usual rotational constants, δ is a Kronecker delta term, and ν_{obs} is the observed transition wavenumber. In Eq. [3] ν_c is the center of the subband. Some workers prefer to use ν_0 defined by

$$\nu_0 = \nu_c + B'k'^2 - B''k''^2, \quad [4]$$

because the ω_i and x_{ij} constants are defined by the ν_0 terms as

$$G_v^0 = \sum \omega_i (v_i + d_i/2) + \sum \sum x_{ij} (v_i + d_i/2) (v_j + d_j/2) + \sum \sum g^{ij} l_i l_j + \sum \sum \sum y_{ijh} (v_i + d_i/2) (v_j + d_j/2) \times (v_h + d_h/2) + \sum \sum \sum y_i^h (v_i + d_i/2) l_i l_h \dots \quad [5]$$

and

$$\nu_0 = G_v^{0'} - G_v^{0''}, \quad [6]$$

where the sums are over the subscripts (and superscripts) with $h \geq j \geq i$ and d is the degeneracy factor, 2 for the bends (ν_4 and ν_5) and 1 for all other vibrational modes. The q_{vj} terms could not be determined from the present measurements and were fixed at values estimated from measurements on other isotopomers (9, 10).

The sextic centrifugal distortion terms (H_v) were not included in Eq. [1] because they were too small to be determined. They are expected to be on the order of -0.032 mHz

(or $-1.1 \times 10^{-15} \text{ cm}^{-1}$) according to the calculations of Botschwina (14).

Only in the case of the $\nu_3 + 2\nu_5 - 2\nu_5$ and $\nu_3 + 3\nu_5 - 3\nu_5$ transitions was it necessary to make a more complicated l -type resonance analysis. For that analysis we used the matrix elements given by Maki and Lide in an earlier paper on HCN (15). Those are the same matrix elements as were given for one bending mode by Herman *et al.* (16) for the case of acetylene, another four-atom linear molecule with the same symmetry as cyanogen.

For the cases with $v_5 > 1$ the displacement of the energy levels due to l -type resonance is dependent on both the coupling constant, q , and the separation of the components with different l values. As a consequence, the analysis of the measurements gives us an indirect way to determine the separation of the $l = 0$ and $l = 2$ states for $2\nu_5$. However, when both the q and the $l = 2, l = 0$ separation were fit, the uncertainty in the value of q was larger than the vibrational dependence and so the value of q for $2\nu_5$ was fixed at an estimated value. For the analysis involving $3\nu_5$, it was assumed that the $l = 1, l = 3$ separation is exactly twice the $l = 0, l = 2$ separation.

If a correction for l -type resonance is not made, its effects are to some extent manifested in effective values for the centrifugal distortion terms. When the centrifugal distortion terms are poorly determined, the fit will give a better estimate of the other constants if the centrifugal distortion term, D , is fixed at a value near that of D_0 and estimated from more accurate measurements. That was done for the $3\nu_5$ hot band. The dependence of D on ν_5 was estimated from the values of the lower state constants measured for ν_3 and for $\nu_3 + \nu_5 - \nu_5$. Table 1 gives the values found from the least-squares analysis of the present measurements. When the D values were not fixed for $3\nu_5$, the constants were within 2σ of those given in Table 1.

The $\nu_1 - \nu_5$ Difference Band

The assignment of the difference band, $\nu_1 - \nu_5$, was fairly straightforward after the lower state rotational constants had been determined from the analysis of the stronger $\nu_3 + \nu_5 - \nu_5$ hot band. The Q branch of this difference band indicated the precise location of the band center and thus verified the J numbering of the P - and R -branch transitions. The

TABLE 1
Constants in Wavenumbers (cm^{-1}) Determined by the Present Analysis

Vib. Transition	ν_c	B'/B''	$D'/D'' \times 10^8$	$q'/q'' \times 10^4$	$q_3'/q_3'' \times 10^{10}$	$J_{\text{max}}/\text{rms dev.}$
$^{15}\text{N}^{13}\text{C}^{13}\text{C}^{15}\text{N}$						
0010 ⁰ 0-0000 ⁰ 0	2079.553 56(14)	0.145 986 0(15) ^a	1.823 5(125)			98
		0.146 464 1(16)	1.830 8(126)			0.0003
0010 ⁰ 1-0000 ⁰ 1	2077.875 51(13)	0.146 473 1(13)	1.927 9(114)	1.988 2(35)	[3.6] ^b	100
		0.146 949 1(13)	1.934 2(118)	2.008 6(35)	[3.6]	0.0006
0010 ⁰ 2-0000 ⁰ 2	2076.215 76(20)	0.146 952 9(32)	1.955 7(341)	1.979 3(12)	[3.1]	80
		0.147 426 5(32)	1.958 0(343)	[2.000]	[3.1]	0.0010
0010 ⁰ 2-0000 ⁰ 2	2076.196 99(20) ^c	0.146 952 9(32)	1.955 7(341)			90
		0.147 426 5(32)	1.958 0(343)			0.0016
0010 ⁰ 3-0000 ⁰ 3	2074.556 77(47)	0.147 430 1(36)	[2.0]	1.860(64)	[2.6]	76
		0.147 902 3(36)	[2.0]	1.873(65)	[2.6]	0.0016
0010 ⁰ 3-0000 ⁰ 3	2074.520 10(46) ^d	0.147 430 1(36)	[2.0]			76
		0.147 902 3(36)	[2.0]			0.0014
0011 ¹ 0-0001 ¹ 0	2076.703 17(32)	0.146 313 3(36)	1.866(40)	1.190(27)	[0.9]	90
		0.146 790 7(36)	1.871(41)	1.192(27)	[0.9]	0.0008
1000 ⁰ 0-0000 ⁰ 1	2018.769 45(41)	0.145 743 2(15)	1.819 7(320)			48
		0.146 949 1(13)	1.934 2(118)	2.008 6(35)	[3.6]	0.0005
$^{15}\text{N}^{12}\text{C}^{13}\text{C}^{15}\text{N}$						
0010 ⁰ 0-0000 ⁰ 0	2098.099 34(16)	0.146 603 2(27)	1.851(57)			62
		0.147 093 4(27)	1.856(57)			0.0004
0010 ⁰ 1-0000 ⁰ 1	2096.350 70(27)	0.147 100 6(100)	1.902(13)	2.230(114)	[3.6]	62
		0.147 588 0(94)	[1.90]	2.250(110)	[3.6]	0.0005

^a The uncertainties in the last digits, twice the standard deviation, are given in parentheses.

^b Constants given in square brackets were fixed during the least-squares fit.

^c The analysis also determined the separation $0000^0 2-0000^0 2 = 2.735 \pm 0.079 \text{ cm}^{-1}$.

^d For the analysis we fixed the separation $0000^0 3-0000^0 3$ at 5.47 cm^{-1} , *i.e.* twice the $l = 2-0$ separation.

TABLE 2
Some Rovibrational Constants (in cm^{-1})
Determined for Cyanogen

	$^{15}\text{N}^{13}\text{C}^{13}\text{C}^{15}\text{N}$	$^{15}\text{N}^{12}\text{C}^{13}\text{C}^{15}\text{N}$
B_0	0.146 464 1(16)	0.147 093 4(27)
α_1	0.000 720 9(14) ^a	
α_3	0.000 479 9(18)	0.000 492 1(5)
α_4	-0.000 326 8(18)	
α_5	-0.000 491 6(22)	-0.000 502 1(8)
γ_{35}	0.000 001 97(80)	[0.000 001 97] ^b
γ_{55}	-0.000 002 69(41)	[-0.000 002 69] ^b
γ^{55}	0.0±0.000 030	[0.00]
x_{35}	-1.687 95(150)	-1.757 82(86)
x_{34}	-2.850 93(122)	
y_{355}	0.004 76(34)	[0.004 76]
y_3^{55}	-0.005 10(18)	[-0.005 10]

^a The uncertainty in the last digits, two standard deviations, is given in parentheses.

^b Numbers enclosed in square brackets were fixed.

spin-dependent alternation in intensity of the transitions was also an important guide and/or verification of the correct rotational assignments. This band was much weaker than the ν_3 band and only the transitions from the lowest possible state, ν_5 , were strong enough to be measured. In our spectrum the strongest transitions of this difference band absorbed only about 1% of the radiation at the center of the strongest lines.

Table 1 gives the constants found from this analysis. If we had a measurement of the ν_5 band, then this measurement of the $\nu_1 - \nu_5$ difference could be used to determine the ν_1 vibrational term value. As it is, the present measurements only determine the rotational constants for ν_1 and the vibrational term value difference $E(\nu_1) - E(\nu_5)$.

The lower state for this difference band is the same as the lower state for the first hot band in the ν_3 band system, $0010^01^1 - 0000^01^1$. Both bands were included in the same least-squares fit so that only one set of constants was determined for the ν_5 level.

RESULTS

The present measurements allow us to determine several rovibrational constants for this heavy isotopomer of cyanogen. Table 2 gives the values for four of the five α_n rotational constants and the two vibrational constants χ_{35} and χ_{34} . The latter terms were determined by making a least-squares fit of the band centers to Eqs. [5] and [6]. In this least-squares fit it was necessary to set most of the constants to zero, and so the ω_i terms are not meaningful and are not given in Table 2. The uncertainties given in Table 2 are those determined by

the least-squares fit and do not reflect errors in the model used for the least-squares fit such as setting higher order terms to zero, or in the case of $^{15}\text{N}^{12}\text{C}^{13}\text{C}^{15}\text{N}$ fixing the y_{355} and y_3^{55} constants at the values found for $^{15}\text{N}^{13}\text{C}^{13}\text{C}^{15}\text{N}$.

The rotational constants given in Table 2 were determined by making a least-squares fit of the B_v values given in Table 1 to the α and γ terms defined by

$$B_v = B_e - \sum \alpha_i (v_i + d_i/2) + \sum \sum \gamma_{ij} (v_i + d_i/2) + \sum \sum \gamma^{ij} l_i l_j, \quad [7]$$

where again the summations are over the quantum numbers with $j \geq i$ and only l_4 and l_5 can be non-zero. Since we had no data for determining α_2 and certain other constants in Eq. [7], the value for B_e given by our least-squares fit was not very meaningful and was not given in Table 2. The uncertainties given in Table 2 were determined by the least-squares fit and did not take into account any model errors.

Most of these constants are very close to what is expected on the basis of the measurements for the same constants for the normal isotopomer (2, 4–6, 9, 10). Unfortunately, we do not have a value for α_2 and are thus unable to determine B_e . We could estimate the value of α_2 from measurements of other isotopomers (1, 8, 17), but the Fermi resonance between ν_2 and $2\nu_4$ is a complicating detail that should first be resolved with greater accuracy. The value of γ_{55} found by Grecu *et al.* (9) seems to indicate that our value is too large by a factor of 2. A refit of their data shows that γ_{55} should be negative when defined by our Eq. [7].

Botschwina and Flügge (17, 18) have used some force field calculations to estimate for several different isotopomers of cyanogen some of the constants given in Tables 1 and 2. Their values are in quite good agreement with ours when the uncertainty in our values is taken into account. For instance, their values for B_0 for $^{15}\text{N}^{13}\text{C}^{13}\text{C}^{15}\text{N}$ and $^{15}\text{N}^{12}\text{C}^{13}\text{C}^{15}\text{N}$ are 4390.88 and 4409.72 MHz, respectively, and our values are 4390.88 ± 0.02 and 4409.75 ± 0.04 where the uncertainty is the standard deviation given by the least-squares fit of the measurements. The agreement for B_0 of $^{15}\text{N}^{12}\text{C}^{13}\text{C}^{15}\text{N}$ can be considered as an additional verification of our assignment, especially the J numbering that cannot be verified by an intensity alternation. The value they calculated (18) for D_0 is $1.845(\pm 0.018) \times 10^{-8} \text{ cm}^{-1}$ and our value is $1.831(\pm 0.006) \times 10^{-8} \text{ cm}^{-1}$.

Our α_n values are also in excellent agreement with the values given by Botschwina and Flügge (17, 18), especially when their values are corrected for the disagreement with the values for the constants for the normal isotopomer ($^{14}\text{N}^{12}\text{C}^{12}\text{C}^{14}\text{N}$) (3, 4, 9, 10). For instance, if we use Grecu's value for ΔB for the normal isotopomer, $\Delta B = B' - B'' = -0.0005334 \text{ cm}^{-1}$, then we find that the mass shift calculated by Botschwina and Flügge (17, 18) gives $\alpha_3 = 0.0004779 \text{ cm}^{-1}$, which is very close to our measured value

of $0.0004799 \pm 0.0000018 \text{ cm}^{-1}$. A similar calculation for α_5 gives $-0.0004863 \text{ cm}^{-1}$, which is close to our observed value $\alpha_5 = -0.0004916 \pm 0.0000022 \text{ cm}^{-1}$.

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