

Infrared Transitions of H¹²C¹⁴N and H¹²C¹⁵N between 500 and 10 000 cm⁻¹

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We have measured the Fourier transform spectrum (FTS) of two isotopomers of hydrogen cyanide (H¹²C¹⁴N and H¹²C¹⁵N) from 500 to 10 000 cm⁻¹. The infrared data have been combined with earlier published microwave and submillimeter-wave measurements. From this analysis new vibration–rotation energy levels and constants are given, based on the observation of a number of new vibrational levels, especially for H¹²C¹⁵N. The Coriolis interaction involving $\Delta v_3 = -1$, $\Delta v_2 = 3$, and $\Delta l = \pm 1$ has been observed for a great many levels and in some cases the assignments of laser transitions allowed by this interaction are more clearly shown. New vibration–rotation constants are given that allow one to predict the transition wavenumbers for most of the transitions below 10 000 cm⁻¹ with accuracies of about 0.5 cm⁻¹ or better. Values are given for the power series expansion of the *l*-type resonance constants and for the centrifugal distortion constants, as well as the usual vibrational and rotational constants. © 1996 Academic Press, Inc.

INTRODUCTION

The spectrum of hydrogen cyanide (HCN) has been of great interest because it is very simple and yet it shows many features that are of interest from a theoretical point of view. The spectrum has been the basis for a number of force field calculations and it is also of interest for comparison with the predictions of *ab initio* calculations. The bending mode of HCN is of particular interest because of the large amplitude of motion for the light hydrogen atom and also because the bending motion is a direct pathway to the HNC isomer. For these applications, it is important to have a list, as complete as possible, of the lowest energy levels including both the vibrational and rotational term values for many isotopomers. A great number of earlier papers have given measurements for many of the lowest vibrational states of HCN but more recent advances in instrumentation have made it possible to provide measurements with greater sensitivity and accuracy.

In recent years there have been several new techniques that allow one to observe very weak transitions or transitions that are not accessible through ordinary absorption spectroscopy techniques (1–5). One of the most promising of these new techniques is the ring-down laser absorption technique (5).

Since the advent of high resolution Fourier transform spectrometers there have been several studies of the high resolution spectrum of hydrogen cyanide (HCN) in rather narrow spectral regions (6–8). In addition, the work of Smith *et al.* (9) covers a wide frequency range that overlaps with the present work. We have recently been involved in an effort to make wavenumber and intensity measurements of the infrared bands of several isotopom-

ers of HCN and DCN (10–12). The present work was undertaken with the view of making a consistent and systematic body of measurements and analyses which would give all the term values available from conventional absorption measurements with state of the art FTS instrumentation for the spectral range from 0 to 10 000 cm⁻¹. Particular attention was given to measuring transitions involving the highest possible value for the bending quantum number. We also give power series constants that can be used to calculate the centrifugal distortion and *l*-type resonance constants for levels that have not yet been observed or whose constants are not well determined. This paper is concerned with only two isotopomers, H¹²C¹⁴N and H¹²C¹⁵N. We also have observed the bands of many other isotopomers both in natural abundance and in isotopically enriched samples and the results of those measurements will be the subject of subsequent papers.

EXPERIMENTAL DETAILS

These measurements were made in Giessen with a Bruker IFS120HR Fourier transform spectrometer which has vacuum transfer optics and various absorption cells. The spectrometer used several different detectors, beam splitters, and optical filters appropriate to the different spectral regions. The resolution of the measurements was close to the Doppler limit and varied from 0.002 to 0.017 cm⁻¹ from the lowest to highest frequency. In many cases the resolution was limited by the pressure broadened linewidths. A multipass long path absorption cell was used for most of the measurements of the normal isotopomer, H¹²C¹⁴N, with a maximum pathlength of about 352 m.

The measurements of $\text{H}^{12}\text{C}^{15}\text{N}$ were made with a smaller White-type borosilicate glass cell with a base length of 0.82 m and a volume of 7 liters. Pressures up to about 5 Torr were used for the measurements of the weakest bands. Higher pressures were not used because of the counter productive effects of pressure broadening and pressure shifts. Even at 5 Torr, the pressure shift might be as large as 0.0008 cm^{-1} (25 MHz) according to the measurements of Smith *et al.* (13). The recent work by Lemaire *et al.* (14) gave a smaller pressure shift, $<0.00041\text{ cm}^{-1}$, at 5 Torr for the ν_2 band. As yet there are not very many good pressure shift measurements against which to test the theory, but many workers now seem to believe that, at least for molecules with large dipole moments, the pressure shift will not be very dependent on either frequency or vibrational state. The band centers were generally determined by measurements at the lowest possible pressure. In addition to affecting the band center measurements, the pressure shifts could also affect the rotational distortion terms, especially H , which are determined by the weak high- J transitions.

The spectra were calibrated using either OCS or CO absorption lines wherever possible. The latest calibration wavenumbers for these gases were used (15). In some cases the wavenumbers of lines of CO_2 or H_2O were used (16). Sometimes it was necessary to use HCN lines from other spectra for the calibration, for instance, when a calibrated run overlapped an uncalibrated run. In many cases different transitions were measured involving the same upper state, but different lower states. Those measurements, when combined with the measurement of the lower state wavenumber separations, gave many different ways of confirming the upper state wavenumbers. This showed us that the calibration for some measurements was less reliable than for other measurements. We believe these problems are due to small phase errors or improper optical alignment for a few spectra. Usually such problems are apparent in slight asymmetries in the lineshapes. These measurements were made over a period of several years and there were many changes in the spectrometer and in the measurement software over that time. When one takes the calibration uncertainties into account, we believe that none of the measurements has an absolute uncertainty smaller than $\pm 0.0003\text{ cm}^{-1}$ even though the statistically determined uncertainties given in the tables may be smaller. A better estimate of the true uncertainty of the measurements would probably be given by adding in quadrature the calibration uncertainty, $\pm 0.0003\text{ cm}^{-1}$, to the statistical uncertainty given in Tables 1 and 3.

ANALYSIS OF THE MEASUREMENTS

In the absence of complications, the absorption lines can be fit by means of the usual energy level polynomials

$$E = G_v + B_v J(J + 1) - D_v [J(J + 1) - l^2]^2 + H_v [J(J + 1) - l^2]^3 \quad [1]$$

and

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

where the single prime (') stands for the upper state and the double prime (") stands for the lower state. In this paper we define a band center, ν_c , such that

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

Some papers define a ν_0 that is identical to our ν_c , while others define a ν_0 such that

$$\nu_0 = \nu_c + (B_v l^2)' - (B_v l^2)'' \quad [4]$$

When a doubly degenerate vibrational state is involved, then vibrational angular momentum, denoted by the quantum number l , must be taken into account. This gives an additional complication due to l -type resonance which is a coupling between levels that have the same quantum numbers, except that the l quantum numbers are different. The most common evidence for l -type resonance is the doubling of the $v_2 = 1$ states which could be viewed as a coupling of the $l = +1$ levels with the $l = -1$ levels. Although weak, this coupling mixes the two levels so that they become two levels of opposite parity whose separation depends on the coupling constant, usually designated as q . Because the levels are of opposite parity, they follow different selection rules for optical transitions. In this paper we use the usual labeling convention (17) which, for HCN, results in the lower energy level for a given J value of a Π state being designated the e level and the upper energy level being designated the f level. The e levels have the same parity as the Σ states. We also use a positive sign for the coupling constant, q . For $v_2 = 1$ states, it is necessary to add to Eq. [1] the term

$$\pm 1/2 [q_v - q_{vJ} J(J + 1) + q_{vJJ} \{J(J + 1)\}^2] J(J + 1), \quad [5]$$

unless one prefers to solve the equivalent 2×2 matrix given below.

When $v_2 > 0$, the allowed values for l are $l = v_2, l = v_2 - 2$, etc. to $l = -v_2$. When $v_2 > 1$, the effect of l -type resonance is more complicated and must be determined by finding the eigenvalues of the energy matrix

TABLE 1
Rovibrational Constants (in cm^{-1}) for $\text{H}^{12}\text{C}^{15}\text{N}$ after Correcting for l -type Resonance

v_1v_2/v_3	G_v^a	B_v	$D_v \times 10^6$	$H_v \times 10^{12}$	J_{max}
0000	0.0	1.435 247 934(87) ^b	2.746 96(45)	2.99(23)	49
0110	711.026 543(25)	1.438 653 063(47)	2.809 16(46)	3.48(27)	45
0200	1409.306 518(46)	1.442 537 933(62)	2.881 72(123)	5.61(75)	41
0220	1424.759 043(47)	1.441 746 516(103)	2.864 59(102)	3.00(75)	40
0310	2110.330 481(48)	1.446 127 307(117)	2.946 660(696)	4.44(60)	39
0330	2141.308 318(207)	1.444 502 711(157)	2.911 081(856)	[3.79] ^c	31
0400	2798.635 046(93)	1.450 231 970(772)	3.025 52(295)	[5.88]	29
0420	2814.184 004(113)	1.449 396 673(803)	3.005 72(160)	[5.28]	30
0440	[2860.782 14]	[1.446 897 0]	[2.950]	[3.48]	
0510	3489.733 095(314)	1.454 034 925(3418)	3.091 55(789)	[6.46]	22
0530	3520.951 790(1003)	1.452 336 0(307)	[3.055]	[5.26]	14
0550	[3583.300 66]	[1.448 904]	[2.98]	[2.86]	
0600	[4167.994 26]	[1.458 376]	[3.169]	[7.34]	
0620	4183.668 96(1827)	[1.457 501]	[3.152]	[6.74]	
0640	[4230.682 38]	[1.454 876]	[3.098]	[4.94]	
0660	[4308.840 23]	[1.450 500]	[3.009]	[1.94]	
0710	4848.989 08(436)	[1.462 412]	[3.240]	[7.93]	
0730	[4880.516 42]	[1.460 620]	[3.200]	[6.73]	
0750	[4943.457 93]	[1.457 035]	[3.130]	[4.33]	
0770	[5037.603 03]	[1.451 658]	[3.030]	[0.73]	
0001	2064.316 149(50)	1.425 579 243(143)	2.752 352(576)	2.91(32)	41
0111	2772.221 950(67)	1.428 870 640(417)	2.812 934(564)	[3.44]	31
1000	3310.089 142(87)	1.425 244 015(399)	2.724 348(609)	3.27(24)	50
0201	3467.783 137(84)	1.432 619 092(875)	2.882 24(149)	[4.33]	37
0221	3482.810 823(120)	1.431 848 987(756)	2.866 124(956)	[3.73]	34
1110	4001.839 711(70)	1.428 857 481(375)	2.793 146(650)	4.37(29)	46
0002	4108.640 172(1135)	1.415 843 19(1642)	2.730 8(382)	[2.78]	21
0311	4166.014 536(168)	1.436 075 47(129)	2.940 24(180)	[4.91]	32
0331	4196.207 054(376)	1.434 488 88(304)	2.904 93(471)	[3.71]	29
1200	4680.812 378(125)	1.432 965 67(109)	2.871 15(219)	4.97(93)	37
1220	4696.095 273(173)	1.432 157 55(106)	2.854 00(189)	[4.97]	37
0112	4813.162 002(920)	1.419 032 97(1520)	2.795 3(508)	[3.36]	18
0401	4851.834 669(293)	1.440 043 71(565)	3.028 4(165)	[5.79]	24
0421	4867.017 816(335)	1.439 223 75(431)	3.000 4(104)	[5.19]	23
0441	[4912.519 07]	[1.436 774]	[2.950]	[3.39]	
1001	5360.254 350(168)	1.415 783 11(113)	2.735 10(140)	[3.40]	29
1310	5362.360 432(165)	1.436 778 25(128)	2.944 84(186)	[5.54]	30
1330	5392.941 608(303)	1.435 120 84(178)	2.905 30(246)	[4.34]	28
1400	6031.203 03(3971)	[1.441 121]	[3.025]	[6.42]	
1420	[6046.547 48]	[1.440 271]	[3.007]	[5.82]	
1440	[6092.483 85]	[1.437 722]	[2.954]	[4.02]	
1111	6049.009 876(448)	1.419 308 61(593)	2.810 9(149)	[3.99]	21
2000	6516.507 348(147)	1.414 945 363(841)	2.703 156(871)	[4.03]	33
1201	6725.247 203(906)	1.423 312 13(1161)	2.892 1(278)	[4.87]	21
1221	[6740.325 45]	[1.422 495]	[2.892]	[4.27]	
2110	7188.798 202(168)	1.418 759 36(156)	2.772 53(302)	[4.61]	27
2200	7848.431 83(316)	1.423 075 5(248)	[2.86]	[5.50]	14
2220	7863.378 91(269)	1.422 201 6(655)	[2.84]	[4.90]	9
2001	8551.184 269(689)	1.405 681 07(553)	[2.72]	[3.95]	16
3000	9621.739 54(113)	1.404 364 25(1332)	2.721 0(286)	[4.57]	22

^a Based on Eqs. [1] and [2] and $G_0 = 0.0 \text{ cm}^{-1}$.

^b The uncertainty in the last digits, twice the estimated standard deviation, is given in parentheses.

^c The values enclosed in square brackets were fixed in the least-squares fit.

used in a new power-series fit. This procedure converged quite rapidly to give the constants reported in the accompanying tables. Since only a few measurements existed for the q_{vJJ} terms, when that term was indeterminate, we fixed it at the value measured for the 01^10 state.

Tables 1 and 3 also give the value for J_{max} which indicates the highest rotational level for which we have measurements. Calculated transition wavenumbers are reliable up to that value of J , but extrapolation beyond J_{max} is not very reliable. One reason that we used fixed values for

TABLE 2
I-type Resonance Constants (in cm⁻¹) for H¹²C¹⁵N

$v_1v_2v_3$	$q_0 \times 10^3$	$q_{vj} \times 10^8$	$q_{vjj} \times 10^{12}$
010	7.069 685 3(41) ^a	8.101 2(62)	1.335(181)
020	7.171 71(119)	8.414 4(739)	[1.3] ^{b,c}
030	7.277 509(112)	9.003 3(359)	[1.3]
040	7.384 986(846)	[9.385]	[1.3]
050	7.499 01(132)	9.950(385)	[1.3]
060	[7.613 0]	[10.31]	[1.3]
070	[7.733 3]	[10.838]	[1.3]
011	7.064 573(489)	8.132 1(777)	[1.3]
021	7.150 18(148)	8.400(162)	[1.3]
031	7.242 336(936)	9.177(149)	[1.3]
041	7.328 36(481)	8.81(116)	[1.3]
110	7.199 748(478)	9.163 4(831)	2.91(36)
120	7.310 97(132)	9.202 2(915)	[1.3]
130	7.430 701(854)	9.960(150)	[1.3]
140	[7.549 9]	[10.33]	[1.3]
111	7.280 20(700)	10.09(226)	[1.3]
121	[7.378 2]	[9.822]	[1.3]
210	7.282 78(190)	8.538(477)	[1.3]
220	[7.413 8]	[10.08]	[1.3]
012	7.056 88(524)	[8.400]	[1.3]

^a The uncertainty in the last digits, twice the estimated standard error, is given in parentheses.

^b Values enclosed in square brackets were fixed for the least-squares fit.

^c For $v_2 > 1$ all data were fit with $\rho = -0.952(78) \times 10^{-8}$ cm⁻¹.

some of the poorly determined higher order constants in the analysis was to ensure that extrapolation beyond J_{\max} would not deviate from reality too quickly. Another reason was to ensure that the other constants are as close to the true values as possible.

Tables 3 and 4 give the rovibrational constants determined for H¹²C¹⁴N. The analysis of the transitions was more complicated for H¹²C¹⁴N because so many vibrational levels were affected by the Coriolis interaction discussed in the next section. Those vibrational states that were not affected by the Coriolis interaction were included in a large least-squares fit of all the present infrared measurements and the earlier reported measurements of microwave and submillimeter-wave measurements (19–22, 29). This analysis was identical to that used for H¹²C¹⁵N as described above.

A separate analysis was made for each pair of vibrational states coupled through the Coriolis interaction. The measurements for those states were analyzed after the best values had been determined for the constants for the lower states involved in the transitions. Those lower state constants were then fixed at the values given in Tables 3 and 4.

**THE ($v_1, v_2, v_3, |J|v_1, v_2 + 3, v_3 - 1, I \pm 1$)
 CORIOLIS COUPLING**

At least 22 laser transitions have been observed for H¹²C¹⁴N and 4 more for H¹²C¹⁵N (31–33). They have been

TABLE 3
 Rovibrational Constants (in cm⁻¹) for H¹²C¹⁴N after Correcting for *I*-type Resonance

$v_1v_2v_3$	G_v^a	B_v	$D_v \times 10^6$	$H_v \times 10^{12}$	J_{\max}
0000	0.0	1.478 221 840(24) ^b	2.910 47(22)	3.40(12)	49
0110	711.979 570(24)	1.481 772 778(108)	2.977 85(28)	4.12(14)	44
0200	1411.413 391(32)	1.485 828 527(151)	3.055 81(45)	5.34(28)	40
0220	1426.529 873(29)	1.484 997 458(123)	3.037 78(39)	4.61(26)	40
0310	2113.450 495(28)	1.489 575 080(143)	3.126 53(43)	5.63(30)	38
0330	2143.760 660(78)	1.487 869 058(557)	3.088 38(142)	4.45(103)	34
0400	2802.958 835(35)	1.493 863 568(391)	3.212 33(106)	7.27(79)	35
0420	2818.175 530(32)	1.492 985 422(349)	3.187 41(99)	5.32(83)	36
0440	2863.781 386(163)	1.490 360 47(242)	3.128 0(81)	[4.51] ^c	18
0510	3495.113 914(125)	1.497 837 723(977)	3.282 68(153)	[7.55]	29
0530	3525.672 428(142)	1.496 030 881(1111)	3.242 81(193)	[6.38]	25
0550	[3586.702 35]	[1.492 429 4]	[3.17]	[4.05]	
0600	4174.608 17(103)	1.502 393 1(179)	3.366 9(557)	[8.56]	18
0620	4189.973 62(68)	1.501 470 1(89)	3.347 2(216)	[7.97]	22
0640	4236.024 69(197)	1.498 679 6(197)	3.276 9(540)	[6.22]	20
0660	[4312.632 84]	[1.494 065 7]	[3.200]	[3.30]	
0710	[4856.694 91]	[1.506 606 8]	[3.44]	[9.27]	
0730	[4887.593 87]	[1.504 711 5]	[3.40]	[8.10]	
0750	[4949.310 36]	[1.500 921 0]	[3.33]	[5.76]	
0770	[5041.681 64]	[1.495 235 0]	[3.22]	[2.26]	
0001	2096.845 570(30)	1.468 142 027(150)	2.916 33(37)	3.30(20)	42
0111	2805.581 924(42)	1.471 574 033(290)	2.983 07(51)	4.19(25)	42
1000	3311.476 834(54)	1.467 798 342(222)	2.885 62(36)	3.62(15)	49
2001	3502.119 705(77)	1.475 493 23(56)	3.057 02(62)	[5.04]	38
0221	3516.871 524(69)	1.474 677 97(39)	3.041 76(39)	[4.46]	34
1110	4004.162 302(41)	1.471 559 956(234)	2.958 35(45)	4.58(21)	43
0002	4173.070 838(83)	1.458 003 52(55)	2.921 78(138)	2.91(90)	37
0311	4201.205 479(42)	1.479 107 65(33)	3.125 28(49)	[5.76]	32
0331	4230.837 077(190)	1.477 425 94(134)	3.089 1(20)	[4.59]	27
1200	4684.310 033(63)	1.475 839 19(54)	3.043 06(104)	5.14(59)	37
1220	4699.208 941(94)	1.474 996 36(66)	3.022 75(126)	5.12(70)	37
0112	4878.295 067(69)	1.461 315 62(65)	2.985 11(175)	2.48(119)	34
0401	4888.038 874(137)	1.483 255 90(146)	3.212 1(40)	[6.76]	26
0421	4902.938 093(222)	1.482 383 26(294)	3.171 9(69)	[6.17]	22
0441	[4947.606 31]	[1.479 798 4]	[3.133]	[4.42]	
1310	5366.875 461(72)	1.479 808 71(45)	3.119 52(60)	[6.09]	30
1330	5396.703 877(152)	1.478 082 01(101)	3.079 05(145)	[4.93]	29
1001	5393.697 713(61)	1.457 934 54(47)	2.894 64(86)	3.80(40)	42
0511	5577.445 07(75)	1.487 100 2(171)	3.315(79)	[7.47]	16
0531	[5607.408 07]	[1.485 300 6]	[3.24]	[6.30]	
0551	[5667.261 51]	[1.481 751 9]	[3.17]	[3.97]	
0202	5571.733 700(118)	1.465 101 96(183)	3.059 31(401)	[4.96]	27
0222	5586.065 168(132)	1.464 302 88(140)	3.045 93(294)	[4.38]	24
1400	6036.962 409(412)	1.484 327 36(653)	3.222 4(202)	[7.09]	20
1420	6051.918 637(409)	1.483 439 53(697)	3.153 6(204)	[6.51]	20
1440	6096.734 393(517)	1.480 787 97(1238)	3.151(73)	[4.78]	13
1111	6083.348 250(50)	1.461 584 82(88)	2.970 13(77)	[4.19]	36
0003	6228.598 299(125)	1.447 807 85(113)	2.929 7(19)	[3.16]	28
0312	6267.665 83(105)	1.468 587 7(70)	3.146(25)	[5.67]	18
0332	6296.516 99(177)	1.466 934 7(157)	[3.091]	[4.51]	15
2000	6519.610 299(74)	1.457 074 009(504)	2.862 17(87)	4.10(38)	44
1510	[6709.498 43]	[1.488 531]	[3.285]	[7.84]	
1530	6739.497 84(1862)	1.486 723 9(197)	[3.247]	[6.67]	
1550	[6799.388 85]	[1.483 085 9]	[3.172]	[4.33]	
1201	6760.704 072(102)	1.465 750 09(121)	3.051 76(218)	[5.33]	32
1221	6775.382 595(183)	1.464 910 53(137)	3.034 60(221)	[4.75]	29
0113	6930.037 64(59)	1.450 994 7(88)	2.986 5(285)	[3.88]	21
0402	6951.683 03(149)	1.472 545(30)	2.977(117)	[6.68]	16
0422	[6966.214 03]	[1.471 728 4]	[3.19]	[6.09]	
0442	[7009.742 25]	[1.469 177 9]	[3.13]	[4.34]	
2110	7192.763 681(67)	1.461 046 82(47)	2.937 48(89)	4.41(45)	38
1311	7440.477 829(81)	1.469 599 76(77)	3.128 60(142)	[6.04]	25
1331	7469.894 53(87)	1.467 880 9(69)	[3.09]	[4.87]	16
1002	7455.423 76(119)	1.448 018 08(823)	2.916 4(90)	[3.53]	18
2200	7853.510 970(129)	1.465 541 33(107)	3.029 45(137)	[5.70]	30
2220	7868.065 178(105)	1.464 700 83(75)	3.006 65(95)	[5.11]	31
1401	8107.968 80(370)	1.473 988 4(302)	[3.21]	[7.04]	15
1421	8122.733 10(338)	1.473 121 7(449)	[3.19]	[6.46]	12
1441	[8167.017 40]	[1.470 498 7]	[3.13]	[4.71]	
1112	8141.731 26(102)	1.451 554 1(194)	2.990(68)	[4.24]	17
2310	8516.469 147(234)	1.469 729 43(286)	3.106 6(68)	[6.41]	22
2330	8545.580 538(394)	1.468 011 78(424)	3.069 6(95)	[5.24]	24
2001	8585.581 071(129)	1.447 429 74(84)	2.871 97(107)	[3.90]	31
1202	8816.003 49(130)	1.455 618 2(218)	3.076(70)	[5.25]	18
1222	[8830.411 56]	[1.454 783 2]	[3.04]	[4.66]	
2111	9256.087 07(38)	1.451 288 3(35)	2.944 2(88)	[4.61]	22
1003	9496.437 17(117)	1.438 029 2(184)	2.908(53)	[3.45]	19
3000	9627.086 91(27)	1.446 033 12(124)	2.838 79(127)	[4.27]	33
2201	9914.399 15(178)	1.455 661 0(180)	[3.04]	[5.61]	14
2221	[9928.823 16]	[1.454 866 3]	[3.02]	[5.03]	
3110	10280.363 55(23)	1.450 226 5(24)	2.915 4(49)	[4.98]	25
3200	10921.444 54(448)	1.454 921(65)	[3.02]	[5.98]	17
3220	10935.596 33(276)	1.454 134(38)	[3.00]	[5.40]	13

^a Based on Eqs. [1] and [2] and $G_0 = 0.0$ cm⁻¹.

^b The uncertainty in the last digits, twice the estimated standard error, is given in parentheses.

^c Constants enclosed in square brackets were fixed for the least-squares fit.

TABLE 4
l-type Resonance Constants (in cm^{-1}) for $\text{H}^{12}\text{C}^{14}\text{N}$

$v_1v_2v_3$	$q_0 \times 10^3$	$q_{\text{vl}} \times 10^8$	$q_{\text{vll}} \times 10^{12}$
0 1 0	7.487 740 0(21) ^a	8.879 3(27)	1.429(37)
0 2 0	7.596 423(180)	9.294 5(219)	1.402(156) ^b
0 3 0	7.709 283(46)	9.883 1(196)	1.623(172) ^b
0 4 0	7.824 082(148)	10.322(21)	[1.4] ^{c,d}
0 5 0	7.945 75(34)	10.879(70)	[1.4] ^d
0 6 0	8.067 78(207)	[11.35]	[1.4] ^d
0 7 0	[8.194 7]	[11.94]	[1.4] ^d
0 1 1	7.479 79(26)	8.818 8(241)	[1.4]
0 2 1	7.575 20(60)	9.192(68)	[1.4] ^d
0 3 1	7.673 860(210)	9.608(37)	[1.4] ^d
0 4 1	7.775 52(109)	[9.814]	[1.4] ^d
0 5 1	7.891 5(25)	[10.42]	[1.4] ^d
1 1 0	7.607 06(28)	9.599(60)	1.88(29)
1 2 0	7.727 18(54)	10.111(56)	[1.4] ^d
1 3 0	7.852 15(28)	10.672(46)	[1.4] ^d
1 4 0	7.968 57(398)	[11.15]	[1.4] ^d
1 5 0	[8.111 4]	[11.73]	[1.4] ^d
1 1 1	7.675 90(101)	10.053(52)	[1.4]
1 2 1	7.778 28(165)	9.961(237)	[1.4] ^d
1 3 1	7.897 71(47)	10.876(105)	[1.4] ^d
1 4 1	[8.009 1]	[11.23]	[1.4] ^d
1 1 2	7.754 6(66)	[10.56]	[1.4]
1 2 2	[7.840 5]	[10.79]	[1.4] ^d
2 1 0	7.694 12(58)	10.170(133)	2.97(73)
2 2 0	7.822 42(141)	10.66(18)	[1.4] ^d
2 3 0	7.957 17(164)	11.43(50)	[1.4] ^d
2 1 1	7.809 2(43)	11.58(134)	[1.4]
2 2 1	[7.962]	[11.43]	[1.4] ^d
3 1 0	7.758 6(30)	10.56(77)	[1.4]
3 2 0	7.807(178)	[11.06]	[1.4] ^d
0 1 2	7.471 66(43)	8.881(58)	[1.4]
0 2 2	7.549 5(32)	9.05(65)	[1.4] ^d
0 3 2	7.628 39(156)	[9.45]	[1.4] ^d
0 4 2	[7.724 9]	[9.67]	[1.4] ^d
0 1 3	7.455 7(94)	7.29(406)	[1.4]

^a The uncertainty in the last digits, twice the estimated standard deviation, is given in parentheses.

^b Also fit was the $l, l \pm 4$ coupling constant, $\rho = -0.1085 (\pm 0.0016) \times 10^{-7} \text{cm}^{-1}$.

^c Values enclosed in square brackets were fixed in the least-squares fit.

^d Fixed in the fit was the $l, l \pm 4$ coupling constant, $\rho = -0.1085 \times 10^{-7} \text{cm}^{-1}$.

shown (30, 34–36) to be based on rotational transitions between adjacent vibrational states that have different populations due to the discharge conditions and a differing rate of collisional relaxation. Those rotational transitions between different vibrational states would normally be extremely weak. However, the mixing of the two vibrational states through a Coriolis interaction causes them to become more nearly like ordinary rotational transitions between levels within the same vibrational state. The most important Coriolis interaction for HCN couples levels that differ by one quantum of ν_3 and three quanta of ν_2 , such as the levels

01^{1e}1 and 04⁰0. It couples levels that have the same rotational J value, but l values that differ by one. The e levels are coupled with other e levels and f levels are coupled with f levels.

Because the rotational constants are quite different for such pairs of levels, there is a high probability that there will be a crossing or near coincidence of the levels at some value of J even if the rotationless band centers are fairly distant. For example, the 02^{2f}1 and 05^{1f}0 levels are 21cm^{-1} apart for the hypothetical $J = 0$ level and yet there is a crossing at $J = 26$. The usual requirement for such a crossing is that the vibrational state with the most bending quanta (which will be the state with the larger rotational constant, B_v) be lower in frequency than the other state. Otherwise, the rotational manifolds are not likely to cross. At the crossing point the rotational levels will be displaced so the separation of the two vibrational states for that J is slightly larger than expected.

In a few cases where the levels are rather widely separated even at the crossing point, the Coriolis interaction may be so widely distributed among several different levels that the closest levels will appear to be closer together when the Coriolis constant is included in the fit. That was found to be the case for the 11^{1e}1–14^{2e}0 interaction where the closest approach is only 0.77cm^{-1} .

In our analysis we have used the same one-step approach to solving the energy matrix as was used in an earlier analysis (35) although we represent the Coriolis term slightly differently. The energy matrix included the complete submatrix for l -type resonance for both vibrational states and the appropriate matrix elements for the Coriolis coupling terms, as illustrated in Eq. [5] of Ref. (35). For the Coriolis coupling matrix element we used the form

$$\langle v_1, v_2, v_3, l | v_1, v_2 + 3, v_3 - 1, l \pm 1 \rangle = \mp W [J(J + 1) - l(l \pm 1)]^{1/2}. \quad [9]$$

From our measurements the Coriolis coupling terms can be determined only from the transitions to those levels that are at a crossing point, or a few higher or lower J values because those are the only levels whose displacement is greater than or equal to the measurement uncertainty. The other transitions can be quite well fit to the usual constants and therefore do not contribute to determining the Coriolis constants.

In several cases two crossing points have been observed for a pair of interacting vibrational levels, (e.g., 03¹1 and 06²0). Even though one crossing involves the e levels and the other involves the f levels, the symmetry of the energy matrix requires that the same interaction matrix element be used for both crossings. Since the measured displacement of the levels seems to require two different values for the interaction constant, we added a J -dependent term to the interaction matrix element such that

TABLE 5
Coriolis Interactions Observed or Expected for H¹²C¹⁴N and H¹²C¹⁵N

levels that are coupled $\nu_1\nu_2\nu_3$ and $\nu_1\nu_2\nu_3$		at the crossing point			Interaction constant	Laser
		J	separation (cm ⁻¹)	displacement (cm ⁻¹)	W (cm ⁻¹)	Observed
H¹²C¹⁴N						
0 1 ^{1e} 1	0 4 ⁰ 0	10	-0.121 85 ^a	0.014 13 ^b	0.002 473 9(15) ^c	yes
0 2 ⁰ 1	0 5 ^{1e} 0	25	0.253 14	0.076 00	0.002 720 8(30)	yes
0 2 ^{2f} 1	0 5 ^{1f} 0	26	-0.192 21	0.065 26	0.002 720 8(30)	yes
0 3 ^{1e} 1	0 6 ⁰ 0	42	[-0.66] ^d			no
0 3 ^{1e} 1	0 6 ^{2e} 0	17	0.137 13	0.000 28	0.000 661(10)	no
0 3 ^{1f} 1	0 6 ^{2f} 0	29	-0.350 53	0.013 75	0.001 878(27)	yes
0 3 ^{3e} 1	0 6 ^{2e} 0	35	[-0.42]			no
0 4 ^{2f} 1	0 7 ^{1f} 0	45	[0.04]			no
0 4 ^{2e} 1	0 7 ^{3e} 0	29	[0.06]			yes
0 4 ^{2f} 1	0 7 ^{3f} 0	23	[0.46]			no
0 2 ^{2f} 2	0 5 ^{1f} 1	16	-0.463 17	0.016 60	0.004 733(45)	yes
1 0 ⁰ 1	1 3 ^{1e} 0	47	[0.39]			yes
1 1 ^{1e} 1	1 4 ^{2e} 0	31	-0.771	-0.002 8 ^e	0.008 10(113)	no
1 1 ^{1f} 1	1 4 ^{2f} 0	45	[0.73]			no
1 2 ^{2e} 1	1 5 ^{3e} 0	44	[0.048]			yes
1 2 ^{2f} 1	1 5 ^{3f} 0	36	[-1.03]			no
1 0 ⁰ 2	1 3 ^{1e} 1	35	[-0.307]			yes
1 1 ^{1e} 2	1 4 ⁰ 1	49	[-0.10]			no
1 1 ^{1e} 2	1 4 ^{2e} 1	24	[0.51]			no
1 1 ^{1f} 2	1 4 ^{2f} 1	34	[0.11]			no
1 2 ^{2f} 2	1 5 ^{1f} 1	49	[0.08]			no
1 2 ^{2e} 2	1 5 ^{3e} 1	34	[0.16]			no
1 2 ^{2f} 2	1 5 ^{3f} 1	29	[0.88]			no
H¹²C¹⁵N						
1 1 ^{1f} 1	1 4 ^{2f} 0	11	0.197 22	0.001 35	0.001 42(31)	no
1 1 ^{1e} 1	1 4 ^{2e} 0	9	0.170 88	0.000 85	0.001 42(31)	no
1 1 ^{1e} 1	1 4 ⁰ 0	32	[-0.390]	0.017 1	0.001 42(31)	yes
0 3 ^{3e} 1	0 6 ^{2e} 0	20	0.395 39	0.016 29	0.003 92(22)	yes
0 3 ^{3f} 1	0 6 ^{2f} 0	25	-0.476 40	0.033 91	0.004 90(15)	yes
0 4 ⁰ 1	0 7 ^{1e} 0	18	0.276 9	0.132 4	0.004 54(4)	no
0 4 ^{2f} 1	0 7 ^{1f} 0	22	0.630 4	0.035 4	0.005 11(14)	no

^a The actual perturbed separation of the energy levels is given for the J at the crossing point. A negative sign indicates that the level on the right is higher than the level on the left at the indicated J value.

^b The displacement is the absolute value of the difference between the perturbed line position and the position calculated assuming the interaction constant is zero for the J value indicated in column 3. No value is given when the interaction constants could not be determined.

^c The uncertainty in the last digits, twice the estimated standard error, is given in parentheses.

^d The square brackets indicate crossings that are outside the range of measured FTS transitions for both levels.

^e A negative displacement indicates that the levels would be farther apart if the Coriolis term were zero, see text.

$$W = W_0 + W_J J(J + 1). \quad [10]$$

However, we cannot be certain that the interaction constant is truly the same for the two interacting rotational manifolds and so in Table 5 we have reported two different values for the interaction constant. Those two values come from our evaluation of Eq. [10]. One could imagine that the e levels might appear to have a different Coriolis

interaction if there were also a weak interaction with a Σ level.

In the case of the interaction between the 05¹0 state and the 02⁰1 and 02²1 states, the crossings are at adjacent J values ($J = 25$ and 26) but states with different l values are being coupled. In this case there is no discernible difference between the two interaction constants so we arbitrarily require that they be the same. In Ref. (35) it was shown that

TABLE 6
HCN Laser Transitions

upper state $v_1 v_2^i v_3$	lower state $v_1 v_2^i v_3$	J'	J''	Observed ^a (cm^{-1})	Calculated (cm^{-1})	Relative Intensity	Ref.
H¹²C¹⁴N							
0 4 ⁰ 0	0 4 ⁰ 0	9	8	26.843 601(17) ^b	26.843 61	0.6	30
0 1 ^{1e} 1	0 4 ⁰ 0	10	9	29.712 579(17)	29.712 57	0.6	30,31
0 4 ⁰ 0	0 4 ⁰ 0	10	9	29.834 446(17)	29.834 42	<0.4	30
0 1 ^{1e} 1	0 4 ⁰ 0	11	10	32.166 033(17)	32.166 02	1	30
0 1 ^{1e} 1	0 1 ^{1e} 1	11	10	32.287 864(17)	32.287 87	0.4	30
0 5 ^{1f} 1	0 5 ^{1f} 1	15	14	44.853(7)	44.851 2	0.08	29
0 2 ^{2f} 2	0 5 ^{1f} 1	16	15	47.393(3)	47.395 0	0.2	29
0 2 ^{2f} 2	0 2 ^{2f} 2	17	16	49.737(8)	49.738 3	0.5	29
0 2 ⁰ 1	0 5 ^{1e} 0	25	24	74.111(10)	74.115 7	0.8	29
0 2 ⁰ 1	0 5 ^{1e} 0	26	25	76.430(10)	76.429 8	4	29
0 2 ^{2f} 1	0 5 ^{1f} 0	26	25	77.743(10)	77.742 2	9	29
0 2 ^{2f} 1	0 5 ^{1f} 0	27	26	79.262(10)	79.262 0	3	29
0 3 ^{1f} 1	0 6 ^{2f} 0	29	28	86.109(8)	86.110	0.5	29
0 4 ^{2e} 1	0 7 ^{3e} 0	30	29	89.233(12)*	89.229	0.2	29
1 3 ^{1e} 1	1 3 ^{1e} 1	34	33	98.759(10)	98.762	0.2	29
1 0 ⁰ 2	1 3 ^{1e} 1	35	34	101.325(4)	101.326	0.8	29
1 0 ⁰ 2	1 0 ⁰ 2	36	35	103.733(13)	103.714	0.2	29
?	?	42?	41?	122.618(14)*		0.1	29
1 2 ^{2e} 1	1 5 ^{3e} 0	44	43	129.868(20)	129.865	0.003	29
1 2 ^{2e} 1	1 5 ^{3e} 0	45	44	131.418(21)	131.423	0.005	29
1 3 ^{1e} 0	1 3 ^{1e} 0	47	46	136.796(17)	136.827	0.008	29
1 0 ⁰ 1	1 3 ^{1e} 0	48	47	139.084(6)	139.077	0.3	29
H¹²C¹⁵N							
0 3 ^{3e} 1	0 6 ^{2e} 0	21	20	60.551(12)	60.556 3	1	29
0 3 ^{3f} 1	0 6 ^{2f} 0	25	24	72.063(9)	72.078 5	1	29
1 4 ⁰ 0	1 4 ⁰ 0	31	30	88.253(24)	88.254 8	0.1	29
1 1 ^{1e} 1	1 4 ⁰ 0	32	31	90.711(14)	90.711 0	1	29

^a The uncertainty in the last digits, twice the estimated standard deviation, is given in parentheses.

^b An asterisk indicates that the measured wavenumber was not included in the analysis.

the expected vibrational dependence for the coupling terms was not obeyed and so we saw no reason to assume any particular vibrational dependence.

Table 5 shows the observed or expected crossings where the Coriolis coupling will be greatest. In some cases the displaced levels have been observed and included in the least-squares fits. In other cases, indicated by square brackets in Table 5, the crossing is expected to occur at rotational levels that are too high to be observed in the present measurements.

Not all of the crossing points given in Table 5 have been observed as laser transitions. In Table 6 we give the observed laser transitions for HCN, their assignments, and the wavenumbers calculated from the constants given in Tables 1 through 4 plus the Coriolis coupling constant if given in Table 5. Most of the weaker laser transitions were only measured in pulsed systems and the wavenumber measurement was not very accurate (31). In those cases where we are certain of the assignments, the wavenumbers of the laser transitions were included in the least-squares analysis.

Fewer examples of this resonance have been found for H¹²C¹⁵N than for H¹²C¹⁴N because of the large displacement of the CN stretching vibration to lower wavenumbers for the ¹⁵N isotopomer. No other examples of level crossings accompanied by either Coriolis or vibrational interactions have been found in our measurements for these two isotopomers. The existence of a $v_1 \pm 2, v_3 \mp 3$ vibrational interaction has already been observed to affect some vibrational levels beyond 10 000 cm^{-1} but we have followed the example of others (9) by not including those perturbed levels in any of this work.

VIBRATIONAL QUANTUM NUMBER EXPANSIONS

The constants given in Tables 1 through 4 were fit to the usual series expansion in the vibrational quantum numbers to determine a new set of constants which would be consistent for the two isotopomers. For the vibrational term values we used the expansion

$$\begin{aligned}
G_v + B_v l^2 + G^0 = & \sum \omega_i (v_i + d_i/2) + \sum \sum x_{ij} (v_i + d_i/2)(v_j + d_j/2) + g_{22} l^2 \\
& + \sum \sum \sum y_{ijk} (v_i + d_i/2)(v_j + d_j/2)(v_k + d_k/2) + \sum y_{ill} (v_i + d_i/2) l^2 \\
& + \sum \sum \sum \sum z_{ijkh} (v_i + d_i/2)(v_j + d_j/2)(v_k + d_k/2)(v_h + d_h/2) \\
& + \sum \sum z_{ijll} (v_i + d_i/2)(v_j + d_j/2) l^2 + z_{llll} l^4,
\end{aligned} \tag{11}$$

where G^0 , which is the zero point energy, is given by the right-hand side of Eq. [11] with all vibrational quantum numbers equal to zero and $l = 0$. This has the effect of setting $G_0 = 0$. In this and the following equations the sums are over all values of the subscript from 1 to 3 (representing the three vibrational normal modes for HCN) with the exception that $h \geq k \geq j \geq i$. As usual, the vibrational degeneracy is given by $d_1 = d_3 = 1$ and $d_2 = 2$. This expansion is the same as that used by Smith *et al.* (9) even though the left-hand side looks different because our Eq. [1] does not include a $-Bl^2$ term and so that term must be added to Eq. [11] to give constants on the right-hand side that agree with standard usage. For comparison with other papers, one should remember that the some workers use x_{il} in place of g_{22} while other workers define g_{22} slightly differently. Our definition of G_v also is different from that of some other workers. With these definitions, the values of G_v given in Tables 1 and 3 are the same as the ν_c for transitions from the ground state to each of the states listed.

The fit used to determine the vibrational constants included 112 different energy levels used to determine the 45 constants for H¹²C¹⁴N. In addition to the measurements given in Table 3, we also included in the fit the SEP measurements beyond 13 670 cm⁻¹, where the calibration is more reliable (1, 2), and the data given by Smith *et al.* (9) and by Romanini and Lehmann (5) for those levels that were not measured in the present work. We also included the measurements by Saury *et al.* (4) and by Baskin *et al.* (3) which were made with their collisional energy transfer technique. Those measurements are not accurate enough to change any of the constants, but they did give a few percent reduction in the uncertainties of some of the constants given in Table 7. No transitions beyond 19 000 cm⁻¹ were included in the least-squares fits.

All the data used in this analysis were weighted by the inverse square of the uncertainty in the measurement. For the present measurements we used an uncertainty that was twice the uncertainty of the G_v values given by the least-squares fits of the individual rovibrational transitions. In most cases, this is too optimistic because there should also be an absolute uncertainty of about ± 0.0003 cm⁻¹ which was not included in the uncertainty. For the SEP measurements we used uncertainties of ± 0.1 cm⁻¹, or greater if so indicated. Smith *et al.* (9) used a weighting scheme that allowed for the model error caused

by the omission of higher order terms because they were most interested in obtaining constants and uncertainties that were more likely to approach the values given by a potential function. We did not use such a weighting scheme because we thought that Fermi resonance should also be included if one were to obtain constants that could be related to a potential function. Instead, we thought it was more important to determine the effective constants needed to calculate unobserved transitions. In fact, earlier versions of these constants allowed us to predict to within 0.05 cm⁻¹ the transitions for several previously unobserved vibrational states and helped to assign some very weak transitions. All of the measurements below 12 000 cm⁻¹ were fit by the constants in Tables 7 to 10 to within ± 0.06 cm⁻¹ and most of the measurements were fit to within ± 0.002 cm⁻¹.

The vibrational constants determined for the two isotopomers are given in Table 7. This table shows that most of the constants are only slightly changed in going from H¹²C¹⁴N to H¹²C¹⁵N. A complete set of all the constants through the z_{ijkh} terms was needed to fit the measurements for the normal isotopomer to within about 10 times the estimated uncertainty of the measurements. The measurements for H¹²C¹⁵N did not extend to such high vibrational quantum numbers; consequently, fewer constants could be determined from the data. We have fixed the values of some of the higher order constants for H¹²C¹⁵N at the values found for H¹²C¹⁴N, in order to allow a more reasonable comparison of the constants for the two isotopomers and also to allow us to extrapolate to higher vibrational states.

Even though very high order constants were included in the fit, the weighted standard deviation of the fit was about 15, for H¹²C¹⁴N, because some of the energy levels were fit with deviations on the order of 15 or more times the uncertainty assigned to the measurements. Most of the lower vibrational states were fit to within one or two times the estimated uncertainty. The largest deviations occur among the higher vibrational states as one might have expected since we know that there are serious model errors in our analysis. The deviations could have been reduced by adding more constants to the fit, but the uncertainty of any added constants was generally equal to, or larger than, the value of the constant. Probably the power series model does not converge very rapidly because it is a poor approximation for the effects of resonances which may get stronger and then weaker as the relative

positions of levels shift with increasing quantum numbers. Since the energy levels are determined with more significant figures than the other rovibrational parameters (except for a few microwave measurements), it is not surprising that they are more poorly fit.

A similar expansion has been used for the rotational constants given in Table 8,

TABLE 7
Constants (in cm^{-1}) for the Vibrational Energy Levels of $\text{H}^{12}\text{C}^{14}\text{N}$ and $\text{H}^{12}\text{C}^{15}\text{N}$

Parameter	$\text{H}^{12}\text{C}^{14}\text{N}$	$\text{H}^{12}\text{C}^{15}\text{N}$
ω_1	3443.080 76(3522) ^a	3441.704 79(2128)
ω_2	726.960 74(843)	725.905 91(858)
ω_3	2127.412 01(4694)	2093.977 71(3074)
x_{11}	-53.203 496(17428)	-53.301 313(8045)
x_{22}	-2.599 847(2606)	-2.622 345(3494)
x_{33}	-10.091 733(37340)	-9.798 489(15242)
x_{12}	-18.939 592(14798)	-18.895 636(9638)
x_{13}	-13.910 718(75360)	-13.631 887(45223)
x_{23}	-3.209 492(9643)	-3.064 251(12780)
g_{22}	5.314 057(2367)	5.364 238(1323)
y_{111}	0.447 836(4467)	0.414 713(1531)
y_{222}	0.021 381(435)	0.022 341(646)
y_{333}	-0.039 269(11589)	[-0.039] ^b
y_{112}	-0.113 845(6114)	-0.086 681(1150)
y_{122}	-0.077 350(2977)	-0.093 593(3768)
y_{113}	-0.464 875(11846)	-0.353 281(2975)
y_{133}	0.157 604(49054)	0.195 201(22777)
y_{123}	0.097 544(14655)	-0.006 565(3502)
y_{233}	-0.120 962(5137)	-0.119 726(5594)
y_{223}	0.092 102(1184)	0.110 244(1991)
y_{11l}	-0.035 176(1840)	-0.034 992(2460)
y_{2ll}	0.004 273(927)	[0.004 3]
y_{3ll}	-0.121 280(2171)	-0.153 293(2751)
z_{1111}	0.009 674 7(3396)	[0.009 67]
z_{2222}	-0.001 298 3(290)	-0.001 313 4(405)
z_{3333}	0.005 774 6(14820)	[0.005 8]
z_{1112}	-0.017 473 0(8295)	[-0.017 5]
z_{1113}	-0.121 055 6(19609)	[-0.121]
z_{1122}	0.014 111 3(5431)	[0.014 1]
z_{1133}	0.051 417 4(43483)	[0.051 4]
z_{1123}	0.093 470 9(3112)	[0.093 5]
z_{1222}	0.001 862 1(2656)	0.003 233 9(5182)
z_{1333}	-0.033 592 6(70450)	[-0.033 6]
z_{1223}	-0.013 256 1(6982)	[-0.013 3]
z_{1233}	-0.036 601 4(58016)	[-0.036 6]
z_{2223}	-0.004 179 3(1044)	-0.005 539 4(2255)
z_{2233}	0.008 255 7(3380)	[0.008 26]
z_{2333}	-0.002 471 0(10081)	[-0.002 5]
z_{111l}	-0.015 507 8(3732)	[-0.015 5]
z_{221l}	0.001 517 9(956)	0.001 312 7(308)
z_{331l}	-0.007 320 5(4493)	[-0.007 3]
z_{121l}	-0.005 405 5(3001)	[-0.005 4]
z_{131l}	0.035 796 0(8066)	0.058 514 5(48664)
z_{231l}	0.005 638 0(3800)	0.007 525 5(3472)
z_{311l}	-0.000 448 9(170)	-0.000 502 4(351)
std. dev. of fit	14.6	7.4
Number of non-zero weighted measurements:	112	43

^a The uncertainty (one standard deviation) in the last digits is given in parentheses.

^b Values enclosed in square brackets were fixed during the fit.

TABLE 8
Rotational Constants (in $\text{cm}^{-1} \times 10^{-3}$) for $\text{H}^{12}\text{C}^{14}\text{N}$ and $\text{H}^{12}\text{C}^{15}\text{N}$

Parameter	$\text{H}^{12}\text{C}^{14}\text{N}$	$\text{H}^{12}\text{C}^{15}\text{N}$
B_e	1484.780 811(2299) ^a	1441.540 564(7402)
α_1	10.435 29(422)	10.012 37(348)
α_2	-3.574 40(216)	-3.424 62(203)
α_3	10.002 84(259)	9.590 65(1904)
γ_{11}	-0.145 020(2408)	-0.142 961(831)
γ_{22}	0.043 053(682)	0.041 065(606)
γ_{33}	-0.029 179(424)	-0.031 238(9501)
γ_{12}	0.195 899(1482)	0.192 617(2133)
γ_{13}	0.196 127(4319)	0.187 909(1953)
γ_{23}	-0.120 675(1565)	-0.112 034(2054)
γ_{ll}	-0.190 750(467)	-0.182 604(396)
γ_{111}	-0.001 552 8(4180)	[-0.001 55] ^b
γ_{222}	0.001 164 5(641)	0.001 066 3(588)
γ_{333}	[0.0]	[0.0]
γ_{112}	[0.0]	[0.0]
γ_{122}	0.003 456 8(3027)	0.004 045 5(4817)
γ_{113}	0.002 739 7(14353)	[0.002 74]
γ_{133}	[0.0]	[0.0]
γ_{123}	0.013 345 8(8253)	[0.013 3]
γ_{233}	[0.0]	[0.0]
γ_{223}	-0.003 234 9(2967)	-0.004 729 9(4566)
γ_{11l}	-0.002 149 0(2340)	-0.004 130 3(4028)
γ_{2ll}	-0.005 849 5(1081)	-0.005 235 4(697)
γ_{3ll}	0.003 416 7(2772)	0.005 021 3(4200)
std. dev. of fit	5.2	3.6
number of non-zero weighted measurements:	82	41

^a The uncertainty (one standard deviation) in the last digits is given in parentheses.

^b Values enclosed in square brackets were fixed during the fit.

$$B_v = B_e - \sum \alpha_i (v_i + d_i/2) + \sum \sum \gamma_{ij} (v_i + d_i/2)(v_j + d_j/2) + \gamma_{ll} l^2 + \sum \sum \sum \gamma_{ijk} (v_i + d_i/2)(v_j + d_j/2)(v_k + d_k/2) + \sum \gamma_{ill} (v_i + d_i/2) l^2, \quad [12]$$

and also for the centrifugal distortion constants given in Table 9,

$$D_v = D_e + \sum \beta_i (v_i + d_i/2) + \sum \sum \beta_{ij} (v_i + d_i/2)(v_j + d_j/2) + \beta_{ll} l^2 \quad [13]$$

and

$$H_v = H_e + \sum \epsilon_i (v_i + d_i/2) + \epsilon_{ll} l^2. \quad [14]$$

Note that here, and later, we have used single, double, and triple subscripts to indicate different orders of magnitude for the constants.

For determining these rotational constants we have used

the constants given in Tables 1 and 3 as well as constants given in the recent papers by Smith *et al.* (9) and Romanini and Lehmann (5). The weights used in the least-squares analysis were based on one standard deviation as given by the present band analysis and three standard deviations for the data taken from the literature.

The measurements of these rovibrational constants are easier to fit with fewer constants but the overall standard deviation of the fits is greater than one because there are many deviations that exceed the uncertainties of the measurements. Again, the constants for the higher energy levels are more difficult to fit to within their uncertainties even though they are often more poorly determined. All of the higher order constants should be treated as effective constants because they will depend on the fixed values used for the next higher order constants. The centrifugal distortion constants are particularly sensitive to any vibrational (or Fermi) resonances and will also depend on how well we have taken into account the effects of *l*-type resonance.

The highest order centrifugal distortion constants, the H_v terms, were very poorly determined (see Tables 1 and 3) and we could only make a very crude estimate of their vibrational dependence, given in Table 9. In the analysis, however, we have used estimated values because we think they are closer to reality than the value zero.

TABLE 9
Centrifugal Distortion Constants (in cm⁻¹)
for H¹²C¹⁴N and H¹²C¹⁵N

Parameter	H ¹² C ¹⁴ N	H ¹² C ¹⁵ N
$D_e \times 10^6$	2.852 97(149) ^a	2.693 21(69)
$\beta_1 \times 10^8$	-3.409 1(1549)	-3.187 7(617)
$\beta_2 \times 10^8$	6.795 7(922)	6.275 6(424)
$\beta_3 \times 10^8$	0.529 6(2084)	0.634 3(823)
$\beta_{11} \times 10^9$	0.494(331)	[0.494] ^b
$\beta_{22} \times 10^9$	0.740(134)	[0.740]
$\beta_{33} \times 10^9$	0.078(606)	[0.000]
$\beta_{12} \times 10^9$	5.577(335)	6.139(363)
$\beta_{13} \times 10^9$	4.575(834)	[4.57]
$\beta_{23} \times 10^9$	-1.700(369)	-2.685(383)
$\beta_{ll} \times 10^9$	-4.643(133)	-4.444(97)
std. dev. of fit	3.8	1.7
number of non-zero weighted measurements:		
	67	37
$H_e \times 10^{12}$	2.458(103)	1.975(195)
$\epsilon_1 \times 10^{12}$	0.284(77)	0.543(228)
$\epsilon_2 \times 10^{12}$	0.857(60)	0.734(147)
$\epsilon_3 \times 10^{12}$	-0.083(105)	[-0.08]
$\epsilon_{ll} \times 10^{12}$	-0.146(47)	[-0.15]
std. dev. of fit	1.4	2.0
number of non-zero weighted measurements:		
	19	9

^a The uncertainty (one standard deviation) in the last digits is given in parentheses.

^b Values enclosed in square brackets were fixed during the fit.

TABLE 10
The Vibrational Expansion Coefficients (in cm⁻¹) for the
l-type Resonance Constants for H¹²C¹⁴N and H¹²C¹⁵N

Parameter	H ¹² C ¹⁴ N	H ¹² C ¹⁵ N
$q_e \times 10^3$	7.229 679(2027) ^a	6.816 059(5199)
$\pi_1 \times 10^3$	0.088 5(33)	0.101 7(96)
$\pi_2 \times 10^3$	0.101 16(79)	0.095 6(22)
$\pi_3 \times 10^3$	-0.018 3(33)	-0.016 4(86)
$\pi_{11} \times 10^4$	-0.162 6(93)	-0.195 5(169)
$\pi_{22} \times 10^4$	0.017 64(111)	0.016 69(328)
$\pi_{33} \times 10^4$	-0.006 8(95)	[-0.006 8] ^b
$\pi_{12} \times 10^4$	0.118 40(542)	0.118 2(109)
$\pi_{13} \times 10^4$	0.790 3(155)	0.862(158)
$\pi_{23} \times 10^4$	-0.137 8(47)	-0.152 1(114)
$\pi_{ll} \times 10^4$	-0.009 0(39)	-0.014(13)
std. dev. of fit	6.5	4.5
number of non-zero weighted measurements:		
	31	16
$q_{eJ} \times 10^8$	7.556(78)	6.742(64)
$\mu_1 \times 10^8$	0.649(142)	0.771(84)
$\mu_2 \times 10^8$	0.528(42)	0.479(25)
$\mu_3 \times 10^8$	-0.185(85)	-0.033(95)
$\mu_{11} \times 10^8$	-0.094(41)	[-0.094]
$\mu_{22} \times 10^8$	0.002 3(52)	[0.002]
$\mu_{33} \times 10^8$	0.056 0(253)	[0.056]
$\mu_{12} \times 10^8$	0.026(22)	[0.026]
$\mu_{13} \times 10^8$	0.465(43)	[0.465]
$\mu_{23} \times 10^8$	-0.108(16)	[-0.108]
$\mu_{ll} \times 10^8$	-0.072(14)	[-0.072]
std. dev. of fit	1.4	3.0
number of non-zero weighted measurements:		
	22	13

^a The uncertainty (one standard deviation) in the last digits is given in parentheses.

^b Values enclosed in square brackets were fixed during the fit.

The *l*-type resonance constants given in Tables 2 and 4 were fit to the expansion

$$q_v = q_e + \sum \pi_i (v_i + d_i/2) + \sum \sum \pi_{ij} (v_i + d_i/2)(v_j + d_j/2) + \pi_{ll} l^2 \quad [15]$$

to obtain the constants given in Table 10, which also gives the next higher *J*-dependent terms given by a least-squares fit to the expression

$$q_{vJ} = q_{eJ} + \sum \mu_i (v_i + d_i/2) + \sum \sum \mu_{ij} (v_i + d_i/2)(v_j + d_j/2) + \mu_{ll} l^2. \quad [16]$$

In Eqs. [15] and [16] we have used an effective value of *l* that is the average of *l* for the two states being coupled, i.e., *l* = 0 for the *l* = +1, -1 interaction and *l* = 1 for the *l* = 0, ±2 interaction.

DISCUSSION

$\Delta l > 1$ Transitions

For both isotopomers a number of unusual $\Delta l > 1$ transitions were observed and included in the present analysis. Such transitions have already been observed in earlier work on HCN (35) and other molecules such as N₂O (37) and C₂H₂ (38). They are usually thought to gain intensity from the l -type resonance between, for instance, $l = 0$ and $l = 2$ states or $l = 1$ and $l = 3$ states. The resonance mixes the two states so that a transition that is normally allowed to the $l = 0$ state will also become allowed to the $l = 2$ state at least for higher rotational levels where the mixing is greater. However, we have also observed a number of Q -branch transitions of the type $l = 2 \leftarrow 0, f - e$, such as 02^2f0-00^00 . They are not allowed, even when the effects of l -type resonance are taken into account, because the resonance does not mix the e and f states. These transitions are an order of magnitude weaker than the $\Delta l = 2$ and $\Delta l = 3$ transitions that are allowed through l -type resonance. Quantitative intensity measurements of those transitions will be the subject of another paper.

High-Order Constants

The higher order constants given in Tables 7–10 are useful for estimating the values of the different rovibrational constants for H¹²C¹⁴N and H¹²C¹⁵N but it is uncertain how accurate those estimates may be. The uncertainties given in the tables are based on the results of a least-squares analysis. Such analyses are reliable only if the model used in the fit is realistic, if the uncertainties used for the data are accurate, and if there is a statistically significant number of measurements. None of those requirements has been fulfilled and that is the reason that the weighted standard deviation of the fits is larger than 1.0. The uncertainties for the constants for H¹²C¹⁵N will be too small because some of the constants were fixed in the least-squares fits. In almost all cases, the uncertainties for the constants for H¹²C¹⁵N should be larger than the uncertainties for the same constants for H¹²C¹⁴N. In some cases the difference in the value of a constant for H¹²C¹⁵N and H¹²C¹⁴N is smaller than the uncertainty in the constant. It is possible that one should use the values found for H¹²C¹⁴N for even more of the H¹²C¹⁵N constants on the assumption that the isotope shift is too small to be measured.

Nakagawa and Morino (39) have published values for the π_{ll} constants that were given by a force field calculation. Their values are quite close to the values given in Table 10.

Our π_{ll} term is nearly equivalent to Watson's q_l^K term (18) and probably should be the same order of magnitude as the q_J term. It could only be determined from measurements of the splitting of Π states and the l -type resonance between Σ and Δ states. For all other examples of l -type resonance the q_l^K term is off diagonal in the energy matrix and couples levels that are too far apart. The uncertainty in

the value of π_{ll} is the same order of magnitude as the value and is also about ten times as large as the q_J term so we do not believe that the value given in Table 10 should be compared with any theoretical value. It may be an artifact created by our model which ignores the effects of vibrational resonances.

Several high-order centrifugal distortion-like constants have been determined with considerable reliability for HCN, notably the H_v terms and the q_{vJJ} and ρ terms; the latter are given in footnotes to Tables 2 and 4. Only a few vibrational transitions were measured to high enough rotational levels to evaluate q_{vJJ} and ρ and so no vibrational dependence could be determined. Enough H_v terms were measured to lead us to believe that we can see their vibrational dependence but the uncertainties are so large that we may only be observing experimental artifacts.

The present value for ρ , the matrix element coupling l with $l \pm 4$, is about half the value found earlier by Maki and Lide (19). This discrepancy is not the result of any difference in the matrix elements; rather, it is because the present analysis includes more high-order terms such as the l dependence of the centrifugal distortion terms and the H_v terms. Adding more terms to an analysis often changes the value of the high-order constants by more than the statistically determined uncertainty. As further evidence that this term is real, the value for H¹²C¹⁵N is slightly smaller than the value for H¹²C¹⁴N and has the same sign. In addition, our determination of ρ from a preliminary analysis of spectra of D¹³C¹⁵N and D¹²C¹⁴N indicates that it is on the order of half the size found for the hydrogen species and also has a negative sign with respect to q , which is given a positive sign for this work. Terms equivalent to our ρ have been observed for acetylene by Sarma *et al.* (40, 41) (and also by earlier workers) and they are also opposite in sign to the q term and have magnitudes close to that of the q_J term.

B_e Constants

For H¹²C¹⁴N the present B_e value of 1.484781 ± 0.000002 cm⁻¹ is not significantly different from the value 1.484773 ± 0.000008 cm⁻¹ given by Winnewisser *et al.* (21). For H¹²C¹⁵N the present B_e value given in Table 8 is also in excellent agreement with the value implied from the r_e values given in Ref. (21).

Check of SEP Assignments

We have used the constants given in Tables 7 and 8 to check the assignments of the stimulated emission pumping (SEP) measurements of Yang *et al.* (1) and Jonas *et al.* (2). When the uncertainty in the SEP measurements is taken into account, our calculated band centers and rotational constants agree with all the assignments of Yang *et al.* and most of those of Jonas *et al.*, but we question the assignments by Jonas *et al.* for the (0, 4^{0,2}, 6), (0, 10^{0,2}, 4), and (2, 10^{0,2}, 1) levels. The (0, 10^{0,2}, 4), (2, 10^{0,2}, 1) levels are predicted

by our constants to be 16 and 25 cm⁻¹ higher, respectively, than the positions given by Jonas *et al.*, while all the other transitions (with two exceptions) up to 19 000 cm⁻¹ are fit to within 2 cm⁻¹ of our calculated position with the highest frequency transitions having the largest deviations. Only a fairly strong vibrational resonance with some other level could displace both of these levels by that much and that seems unlikely. Even the well-known resonance between the (2, 0⁰, 4) and (4, 0⁰, 1) levels, which are separated by less than 3 cm⁻¹, displaces those levels by no more than 8.5 cm⁻¹. The correct assignment for four of the six levels in question would seem to be $G(0, 4^0, 6) = 14\,992.06$ cm⁻¹, $G(0, 4^2, 6) = 15\,004.54$ cm⁻¹, $G(0, 10^0, 4) = 15\,002.13$ cm⁻¹, and $G(0, 10^2, 4) = 15\,016.861$ cm⁻¹, which agrees with Carter *et al.* (42). We also believe that the other two levels are probably $G(3, 2^0, 2) = 14\,987.01$ and $G(3, 2^2, 2) = 15\,000.81$ cm⁻¹ although we have no explanation for the intensity of the SEP measurements. The former four levels have the $l = 0, l = 2$ energy level separation that we calculate, while the latter two have a separation that is too small by 0.4 cm⁻¹. For the other assigned energy levels our calculated separation of the $l = 0$ and 2 levels is within 0.27 cm⁻¹ of the separation measured by SEP. This good agreement leads us to believe that the accuracy of this difference measurement is not affected by the calibration uncertainty of 2 cm⁻¹ suggested by Yang *et al.* for those SEP measurements below 13 670 cm⁻¹.

Another important criterion for the assignments is the B value for the state. The SEP measurements give B values that are consistently larger than the values that we calculate. That is also the case for our suggested assignments but is not the case for the two Jonas *et al.* assignments involving $v_1 = 2$. As indicated by Jonas *et al.* a weak resonance could affect the apparent B_v values so this argument is not at all conclusive.

Jonas *et al.* suggested that the intensity and therefore the observation of the (2, 12^{0,2}, 2) level is due to mixing with the nearby (0, 12^{0,2}, 5) level through the $\Delta v_1 = \pm 2, \Delta v_3 = \mp 3$ resonance which also couples the (2, 0⁰, 4) and (4, 0⁰, 1) levels. Evidence of this interaction is provided by the separation of the $l = 0$ and $l = 2$ levels. The 15.07 cm⁻¹ separation of the $G(2, 12^{0,2}, 2)$ levels is smaller than the predicted value 15.31 cm⁻¹ and the 15.10 cm⁻¹ separation of the $G(0, 12^{0,2}, 5)$ levels is larger than the predicted value of 14.83 cm⁻¹. The B values also seem not to agree although the sum of the B values for the two states is close to the calculated value. In this case the resonance between these levels is certain to be important and is complicated by a low- J crossing of the rotational manifolds of these levels. Especially important for this level crossing is the larger B value expected for the state that is at lower frequency. As the separation of the interacting levels diminishes with increasing values of J , there will be an increase in the effect of the resonance. For instance, if the unperturbed separation of the levels is the same as the observed separation of the

band centers, 3.2 cm⁻¹, then the two vibrational states will be exactly coincident between $J = 11$ and $J = 12$, according to our calculated unperturbed B values, $B(0, 12^0, 5) = 1.470875$ cm⁻¹ and $B(2, 12^0, 2) = 1.493760$ cm⁻¹, and ignoring the l -type resonance which will be nearly the same for both states. Since the unperturbed separation of the two states is certain to be smaller than the observed separation, the crossing should occur at even lower J . Both of these levels, and their $l = 2$ companions, will also move into coincidence with the (0, 6^{0,2}, 7) levels between $J = 14$ and $J = 18$, depending on the levels involved.

For these higher vibrational states where the rotational levels of one vibrational state will come close to and cross the rotational levels of another vibrational state, the correct vibrational assignments can only be understood when all interacting levels are included in a perturbation analysis. In many cases nearby vibrational states will not have large enough interaction matrix elements to affect the energy levels and intensities, but in the cases cited above the interaction seems not to be trivial and the mixing of the energy levels will be strongly J -dependent because the separation of the energy levels is strongly J -dependent.

Observed and Expected Coriolis Interactions

Of the 23 examples of level crossings and accompanying Coriolis interactions given in Table 5 for H¹²C¹⁴N, 9 of them are responsible for 21 laser transitions. Some of the crossings we have located are at rotational states beyond the range of the present measurements, but seven points of interaction have been directly verified by the observation of transitions that are slightly displaced from the expected position.

In some cases where the observed displacement is less than 0.01 cm⁻¹, the value of the interaction constant and its uncertainty are poorly determined. Only a few measurements of small displacements of weak transitions do not give much confidence in the interaction analysis. From these measurements the vibrational dependence of the Coriolis interaction constant does not seem to be systematic and may be partially obscured by experimental error. In an analysis of the spectrum of H¹³C¹⁴N to be published later we have observed the same Coriolis interaction between 05¹⁰ and 02^{2e1} and 02^{2f1} and find that the interaction constant ($W = 0.002493 \pm 0.000008$ cm⁻¹) is nearly the same as that observed for H¹²C¹⁴N.

The four laser transitions for H¹²C¹⁵N were used in the least-squares fits and are responsible for determining the position of the 06²⁰ and 14⁰⁰ states as well as improving our knowledge of some other constants. The FTS transition measurements extended beyond the Coriolis crossing points for the 03^{3e1}, 03^{3f1}, 04⁰¹, and 04^{2f1} states so that we can be certain that the crossing does exist at the J values given in Table 5. The low- J crossings of the 11¹¹ state with the 14²⁰ state were observed in a spectrum of the 11¹¹-00⁰⁰ band in a sample that was not enriched in ¹⁵N. Those lines

were so weak and the perturbation caused such a small shift that the Coriolis interaction constant was poorly determined. Furthermore, no transitions were observed for either the 14^{00} or 14^{20} states with the exception of the two laser transitions.

The $P(19)$ and $R(17)$ $07^{1e0}-02^{00}$ transitions have been observed even though no other transitions involving 07^{10} were found. Those transitions have nearly the same intensity as the $04^{01}-02^{00}$ transitions because the Coriolis mixing of the levels is nearly 50:50 at $J = 18$. The strong Coriolis mixing is also shown by the very small difference between the perturbed separation and twice the displacement of the levels; see Table 5.

Because of the symmetry of the energy matrix, the same term describes the coupling of the 03^{3e1} and 06^{2e0} levels and the coupling of the 03^{3f1} and 06^{2f0} levels. In order to allow for a small difference between the effective Coriolis constants for those two interactions, a J -dependent Coriolis term was included in the fit. The fit then gave $W = (0.2146 \pm 0.0356) \times 10^{-2} + (0.424 \pm 0.061) \times 10^{-5} J(J + 1)$ which is equivalent to the values given in Table 5 at $J = 20$ and $J = 25$.

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