

Intensity Measurements of $\Delta l > 1$ Transitions of Several Isotopomers of HCN

Arthur Maki,* Wolfgang Quapp,† Stefan Klee,‡ Georg Ch. Mellau,‡ and Sieghard Albert‡,¹

*15012 24 Avenue S.E., Mill Creek, Washington 98012-5718; †Mathematisches Institut, Universität Leipzig, Augustus-Platz 10-11, D-04109 Leipzig, Germany; and ‡Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 58, D-35392 Gießen, Germany

Received May 29, 1997; in revised form July 21, 1997

The intensities of the forbidden Q -branch transitions $02^{2f}0-00^0_0$, $12^{2f}0-00^0_0$, and $02^{2f}1-00^0_0$ for HCN have been measured. The intensities of the $02^{2f}0-00^0_0$ transitions of DCN, $D^{13}C^{15}N$, and $H^{12}C^{13}N$ were also measured, as well as the $02^{2f}1-00^0_0$ transitions of $H^{12}C^{15}N$ and $H^{13}C^{15}N$. These Q -branch transitions are forbidden even when the effects of l -type resonance are considered so they must get their intensity from some other Coriolis interactions. The much stronger P - and R -branch lines for the e levels of these same vibrational transitions were also measured and they are shown to get most of their intensity from l -type resonance. However, the same Coriolis resonance that gives intensity to the Q -branch transitions seems to affect the $\Delta J = \pm 1$ transitions as shown by the difference in the intensities of the $\Delta J = +1$ and $\Delta J = -1$ transitions. Measurements of the intensity of the $03^{3e}0-00^0_0$ and $03^{3f}0-00^0_0$ transitions shows that they derive most, but perhaps not all, of their intensity from l -type resonance. An unsuccessful search for forbidden $\Delta J = 0$, $e-e$ transitions for the strong $10^0_0-00^0_0$ band shows that there is no detectable mixing of the e and f levels. © 1997 Academic Press

INTRODUCTION

Infrared intensity measurements of weak transitions can be a sensitive way to observe weak interactions as was shown in our analysis of the Herman–Wallis effect for the very weak CN stretching fundamental band of HCN (I). In other papers (2, 3) it has been shown how the mixing of levels through l -type resonance can have a significant effect on the J -dependence of the intensity. In the case of normally allowed transitions, l -type resonance modifies the normal J -dependence of the intensity creating a so-called Herman–Wallis effect. In a number of papers the intensity also has been used to help in determining the degree of mixing of vibrationally coupled levels. This is particularly useful when only one “bright state” is involved and the intensity can be assumed to be entirely due to interactions with that state. A good example of that was the analysis of the mixing of the 20^0_8 , 60^0_2 , and 72^0_0 levels in $HC^{15}N$ by Romanini and Lehmann (4).

It is particularly useful to study transitions that are forbidden by the normal selection rules because, if any intensity at all is observed, it must be due to some interaction that enables the transition to borrow intensity from an allowed transition. For this paper we measured, apparently for the first time, the intensity of forbidden $\Delta l = 2$ Q -branch transitions of the type $X2^{2f}Y-00^0_0$ where the intensity must be borrowed from some distant allowed transition. That inten-

sity borrowing also affects the intensity of the $X2^{2e}Y-00^0_0$ transitions although it is somewhat masked by the stronger effect of l -type resonance.

We also have made measurements of the $\Delta l = 3$ transitions involving the $03^{3f}0-00^0_0$ Q branch, as well as the $03^{3e}0-00^0_0$ P and R branches. These $\Delta l = 3$ transitions get most of their intensity through l -type resonance which mixes the 03^3_0 and 03^1_0 states. This work shows, through the agreement of the calculated and observed intensity, that we really do understand how that transition gets most of its intensity. It has been suggested that the nearby ν_3 level may perturb the 03^1_0 state but the effects of that interaction must be very small because they are not seen in the present measurements.

We have also sought to observe forbidden $\Delta J = 0$, $e-e$ transitions for the $10^0_0-00^0_0$ band of HCN, to see if there is any detectable mixing of these e levels with the f levels of some other band in the field-free low-pressure environment of these measurements. In this paper we denote the CH stretching fundamental as ν_1 and the CN stretching fundamental as ν_3 . Our failure to observe any forbidden Q -branch transitions for the ν_1 band shows that there is no sign of a mixing of the e and f levels which also might have explained some of the intensity of the $\Delta l = 2$ and $\Delta l = 3$ transitions.

EXPERIMENTAL DETAILS

This work is based on spectra measured on the Bruker IFS120HR interferometer in the Giessen laboratory. This

¹ Present address: Department of Physics, 174 West 18th Avenue, Columbus, OH 43210-1106.

instrument was equipped with vacuum transfer optics and various light sources, beam splitters, optical filters, and detectors to yield optimum instrumental performance in the different spectral regions. The measurements were made with an unapodized instrumental resolution that was less than the Doppler width of the lines. The spectra were measured at pressures between 1 and 5 mbar as determined with a capacitance pressure gauge (MKS baratron). Most of the measurements involved weak features for which instrumental distortion and saturation effects were negligible. The measurements of most of the heavy atom isotopomers were made with a White-type borosilicate glass cell having a base length of 0.82 m and a volume of about 71. This cell was set for a path length of 19.68 m for most of the measurements. For the measurements of the 02^20-00^00 band of $\text{H}^{12}\text{C}^{14}\text{N}$ and $\text{H}^{12}\text{C}^{15}\text{N}$ the cell was set for a path length of 13.12 m. The weakest bands of the normal isotopomer were measured with a stainless steel White-type multipass cell with a base length of 4 m. This cell was set for a path length of 192 m near 3516 cm^{-1} and 240 m near 4698 cm^{-1} .

In addition to using a sample of HCN with the normal isotopic abundance, we also used a sample consisting of about 98% $\text{H}^{13}\text{C}^{15}\text{N}$ and another sample with 95% $\text{H}^{12}\text{C}^{15}\text{N}$, 1% $\text{H}^{13}\text{C}^{15}\text{N}$, and 4% $\text{H}^{12}\text{C}^{14}\text{N}$. The measurements of DCN were made with a sample that contained 99% deuterium but one can expect that exchange with residual water in the system would result in a spectrum with a slightly smaller effective deuterium content. The $\text{D}^{13}\text{C}^{15}\text{N}$ measurements were made with a sample enriched to about 98%.

DESCRIPTION OF THE FORBIDDEN TRANSITIONS

The normal selection rules for spontaneous electric dipole transitions for a linear triatomic molecule are

$$\Delta J = 0, \pm 1, \Delta l = 0,$$

except that $\Delta J = 0$ is not allowed for $l = 0$, and

$$\Delta J = 0, \pm 1 \text{ for } \Delta l = \pm 1.$$

The rovibrational energy levels for HCN can be classed as either e or f levels according to the parity of the levels as described by Brown *et al.* (5). This classification forms the basis for an even more rigid selection rule that for $\Delta J = 0$ only $e \leftrightarrow f$ transitions are allowed and for $\Delta J = \pm 1$ only $e \leftrightarrow e$ and $f \leftrightarrow f$ transitions are allowed. If there were any mixing of the e and f levels, then the selection rules would appear to be violated.

Coriolis interactions can couple certain levels that have different amounts of vibrational angular momentum, different l . That coupling results in a mixing of the wavefunctions of the levels and may result in levels for which the value of l is not well defined. If l is poorly defined, then any selection

rules on l cannot be rigidly obeyed. Coriolis interactions do not result in any mixing of the e levels with the f levels.

The most common form of Coriolis interaction is l -type resonance which gives intensity to the P - and R -branch transitions that we observed in HCN for the 02^20-00^00 , 12^20-00^00 , and 02^2e1-00^00 bands. A quantitative fit of the intensities of these transitions shows that, as expected, their transition dipole moment goes to zero for the lowest rotational transitions, and the J -dependence of the transition dipole moment is so great that the intensity maximum for both P and R branches occurs at about $J = 18$, which is much higher than that for a normal band where the maximum is at about $J = 8$. The intensity of these transitions can be understood as arising from a mixing of the $X2^0Y$ levels with the $X2^eY$ levels. Since that mixing cannot give intensity to the $X2^fY-00^00$ transitions, it was surprising to find the Q -branch transitions due to 02^2f0-00^00 , 12^2f0-00^00 , and 02^2f1-00^00 . It was not surprising, however, to find that those transitions are considerably weaker than the corresponding $\Delta l = 2$, $e-e$, P - and R -branch transitions. Figure 1 shows the spectrum in the region of the 02^2f0-00^00 Q -branch transitions. Figures 2 and 3 show the spectra in the regions of the other two Q branches. The latter two are much weaker because they involve changes of three vibrational quanta, rather than two.

In two spectra made with enriched samples of $\text{H}^{12}\text{C}^{15}\text{N}$ we also have observed the transitions 02^2f0-00^00 and 02^2f1-00^00 for that isotopomer and we have a spectrum of $\text{H}^{13}\text{C}^{15}\text{N}$ in which the 02^2f1-00^00 transitions are just barely visible. In spectra of DCN and $\text{D}^{13}\text{C}^{15}\text{N}$ the 02^2f0-00^00 transitions have also been observed but they seem to have intensities that are weaker than the same transitions for HCN by a factor of 4 to 6. Since the signal to noise ratio was less favorable, a good measurement of the intensities for the deuterated species was not possible. All of these Q branches had intensity maxima at $J \sim 16$, perhaps a little higher for DCN. A normal $\Delta l = \pm 1$ Q branch would have an intensity maximum at $J \sim 8$ while a $\Delta l = 0$ Q branch is strongest for the lowest J transition, $J = 1$ for a $\pi-\pi$ transition.

We have also measured the intensities of the forbidden P - and R -branch transitions for 03^3e0-00^00 and the Q -branch transitions for 03^3f0-00^00 . In both these cases the $\Delta l = 3$ transitions are allowed because of the mixing due to l -type resonance between the 03^10 and 03^30 states. In this case one would expect the Q -branch transitions to be stronger than the P - and R -branch transitions as is found for a normal perpendicular transition. The lines of these bands have a maximum intensity at $J \sim 19$ and the Q -branch transitions are more than twice the intensity of the R -branch transitions. The R -branch transitions were reported earlier (6) although no intensity measurements were made.

If there were any mixing of the e and f states then any transition that is allowed to an e state would also be allowed to an f state and vice versa. This would mean that since the

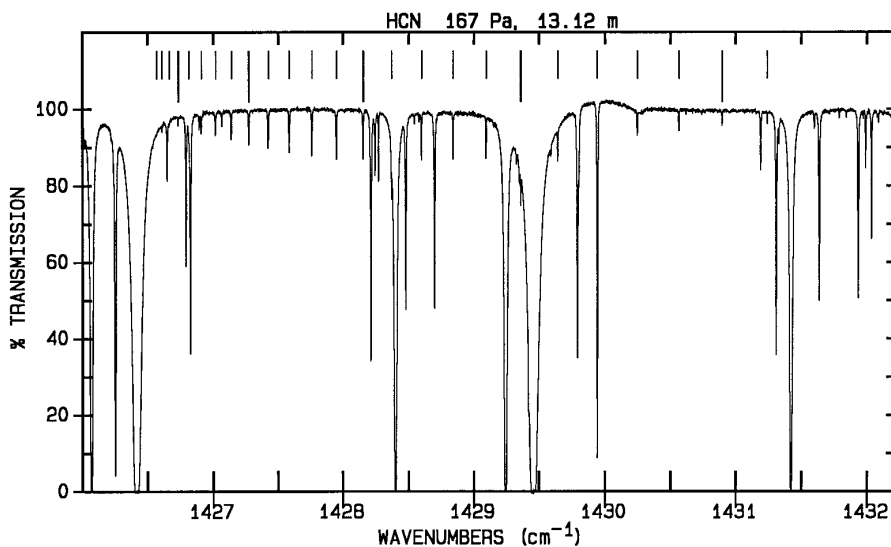


FIG. 1. Spectrum in the region of the Q -branch transitions for the $02^2_0-00^0$ band of HCN. The tick marks at the top indicate the positions of the transitions. The J values divisible by 5 are indicated by longer tick marks. The band center is at the left-hand side of the figure.

02^{2e}_0 and 02^0_0 states are mixed by l -type resonance, then the 02^{2f}_0 and 02^0_0 states would also be mixed. It also would mean that $e-e$ Q -branch transitions would be possible. To test this latter possibility, we have tried to observe Q -branch transitions for the $10^0_0-00^0_0$ band near 3311 cm^{-1} . Our failure to observe such transitions means that they must have transition dipole moments smaller than 1.5×10^{-4} D or intensities that are less than 4×10^{-6} times the intensity of the normally allowed transitions. These measurements were made in a field-free environment at a pressure of 1 mbar and a path length of 192 m.

ANALYSIS OF THE DATA

The assignment of the transitions was based on earlier published and unpublished analyses of a great number of allowed transitions for $\text{H}^{12}\text{C}^{14}\text{N}$ (7), $\text{H}^{12}\text{C}^{15}\text{N}$ (7), $\text{H}^{13}\text{C}^{15}\text{N}$ (8), $\text{D}^{12}\text{C}^{14}\text{N}$ (8, 9), and $\text{D}^{13}\text{C}^{15}\text{N}$ (8, 9). We are confident that the transitions have been correctly identified because the measured transition wavenumbers agreed with the calculated wavenumbers to within the estimated uncertainty of about $\pm 0.0006\text{ cm}^{-1}$ for individual line measurements of a nearly complete series of Q -branch transitions.

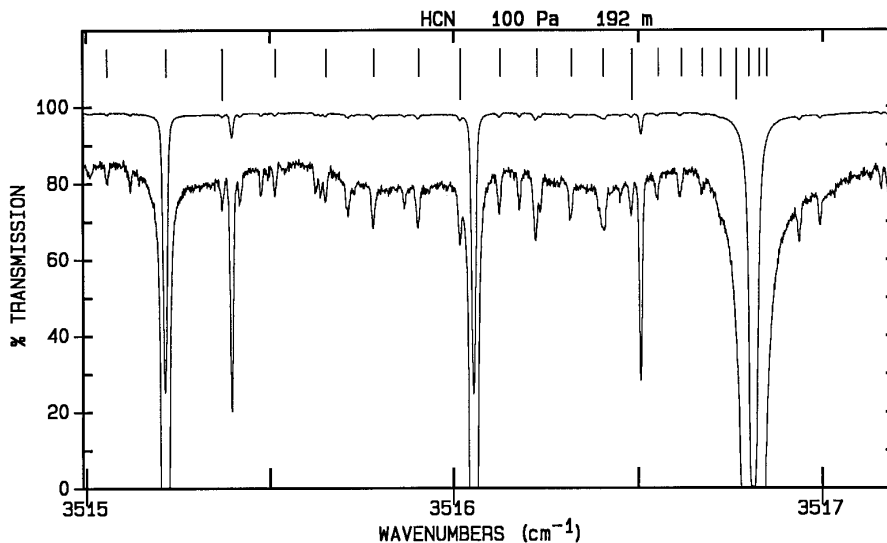


FIG. 2. Spectrum in the region of the Q -branch transitions for the $02^2_1-00^0$ band of HCN. The % transmission scale applies to the upper curve. The lower curve is the same spectrum on a transmission scale expanded by a factor of 10 so that it ranges from a maximum of 100% transmission to a minimum of 90% transmission. The tick marks indicate the location of the Q -branch transitions. The band center is on the right-hand side of the figure.

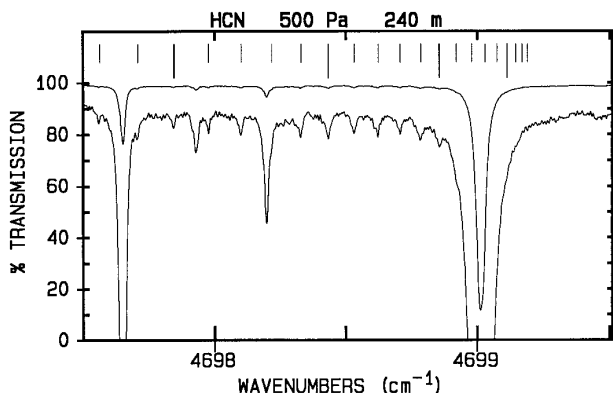


FIG. 3. Spectrum in the region of the Q -branch transitions for the 12^{20} – 00^0 band of HCN. The % transmission scale applies to the upper curve. The lower curve is the same spectrum on a transmission scale expanded by a factor of 10 so that it ranges from a maximum of 100% transmission to a minimum of 90% transmission. The tick marks indicate the location of the Q -branch transitions with the longer tick marks indicating the J values divisible by 5. The band center is on the right-hand side of the figure.

The intensity of each line was determined by a nonlinear least-squares fit of the line profile using the fitting program INTBAT developed by Johns and co-workers (10, 11) and used in our earlier intensity measurements (1, 3). This program fits the lineshape to a Voigt profile that has been convolved with an instrument function. The profile of each line was fit to five parameters, the background 100% transmission level, the slope of the 100% transmission level, the center position of the line, the linewidth, and the line intensity. The line intensity, S_m , is defined by

$$S_m = p^{-1}l^{-1} \int k_\nu d\nu, \quad [1]$$

where p is the HCN pressure, l is the absorption pathlength, k_ν is the absorption coefficient at wavenumber ν , and the integration is over the entire absorption line. The absorption coefficient is given by

$$k_\nu = \ln(I_0/I)_\nu.$$

The analysis avoided using lines for which the peak absorptions were greater than 70% ($k_\nu > 1.2$). This paper deals with transitions that are forbidden in the absence of rotation, which means that the rotationless transition dipole moment is zero. Consequently the line intensities were used to determine a transition dipole moment function given by

$$R^2 = (S_m 3hc Q_r Q_v T) / 8\pi^3 \nu_m 273.15 \times La \exp[-E''/kT](1 - \exp[-\nu_m/kT]), \quad [2]$$

where Q_r and Q_v are the rotational and vibrational partition functions, L is Loschmidt's number, E'' is the energy of the

lower state rovibrational level, T is the temperature (kelvin), a is the isotopic abundance of the species being considered, k is the Boltzman constant, and ν_m is the wavenumber of the center of the line. The Hönl–London terms have been included in the squared transition dipole term, R^2 . To allow for the possibility that the effective transition dipole may have contributions from several sources, it was defined as a sum of several terms as

$$R = L_1 C_1 F_1(J) + L_2 C_2 F_2(J) + \text{etc.}, \quad [3]$$

where L_i is the Hönl–London factor and $F_i(J)$ is a function of J . Their form is determined by the perturbations that contribute the intensity factors C_i , as will be described later. With this definition the constants C_i may be given in debye units. The relative signs of the transition dipole moment constants, C_i , can be determined from the present measurements even though their absolute signs cannot be determined at this time. Table 1 gives the partition functions and some other molecular properties used in this analysis. Tables 2 and 3 give the measured $\Delta l = 2$ line intensities for those bands for which good Q -branch intensity measurements were made. Table 4 gives the measured line intensities for the two deuterated isotopomers for which the Q -branch intensities were poorly determined. The observed – calculated (O – C) values given in Tables 2 to 4 were given by the least-squares fit that gave the constants labeled “obs.” in Table 5.

We shall show in the next sections that a reasonable form for Eq. [3] for the $\Delta l = 2$ transitions is

$$R = L_1 \{ C_1 + C_2 J'(J' + 1) \} \{ J'(J' + 1) - 2 \}^{1/2} + L_2 \{ C_3 + C_4 J'(J' + 1) \} \times \{ J'(J' + 1)[J'(J' + 1) - 2] \}^{1/2}. \quad [4]$$

For P - and R -branch transitions the Hönl–London terms were

$$L_1 = \frac{1}{2}(J' - J'')(3J' - J'' + 1)^{1/2} \quad [5]$$

and

$$L_2 = [(J' + J'' + 1)/2]^{1/2},$$

while for Q -branch transitions we used

$$L_1 = [(2J + 1)/2]^{1/2}$$

and

$$L_2 = 0.$$

It is important to note that the sign of L_1 in Eq. [5] is not

TABLE 1
Some Constants Used in This Work

	HCN	HC ¹⁵ N	H ¹³ C ¹⁵ N	DCN	D ¹³ C ¹⁵ N
Vibrational Transition Dipole Moments (debye):					
$R(01^0-00^0)$	0.189			0.104	
$R(01^1-00^0)$	0.00824(5) ^a {40} ^b				
$R(11^0-00^0)$	0.00986(11){50}				
$R(02^0-00^0)$	0.0496	0.0496	0.0496	0.0234(4){12}	
$R(12^0-00^0)$	0.000795				
$R(02^01-00^0)$	0.00334	0.00381(6){19}			
$R(03^0-00^0)$	0.00326				
$R(03^0-01^0)$	0.0473				
Partition functions:					
$Q_v(298\text{ K})$	1.0676	1.0680	1.0701	1.144	
$Q_v(296\text{ K})$	1.0660	1.0664	1.0685	1.141	1.145
$Q_t(298\text{ K})$	140.45	144.64	148.66	171.83	
$Q_t(296\text{ K})$	139.51	143.68	147.66	170.68	178.94

^a Uncertainties are given for the transition dipole moments in those cases where they are given for the first time. The uncertainties given in parentheses resulted from a least-squares fit of the line intensities.

^b The curly brackets, {}, indicate the uncertainty in the last digits due to uncertainty in the partial pressure measurement.

the same for the P -branch and R -branch transitions. Consequently, the terms with C_1 and C_2 either add to, or subtract from, the terms with C_3 and C_4 depending on whether $\Delta J = +1$ or $\Delta J = -1$. The form of Eq. [3] used for the $\Delta l = 3$ transitions will be given later. Table 5 gives the constants determined by a least-squares fit of the observed line intensities to Eq. [4]. The $O - C$ values given in Tables 2 to 4 were the deviations given by the least-squares fit that determined the constants given in Table 5.

Intensity Contribution from l -Type Resonance for $v_2 = 2$

To calculate the mixing of the wavefunctions due to l -type resonance, one must find the eigenvectors for the energy matrix that includes the matrix elements for l -type resonance. If $v_2 = 2$, the energy matrix with l -type resonance for a given value of J is given by

$$E = \begin{vmatrix} E(X2^2Y) & W_{20} & W_{2-2} \\ W_{02} & E(X2^0Y) & W_{0-2} \\ W_{-22} & W_{-20} & E(X2^{-2}Y) \end{vmatrix}, \quad [6]$$

where the unperturbed wavenumber of the energy level is given by

$$E = G_v + B_v J(J+1) - D_v [J(J+1) - l^2]^2 + H_v [J(J+1) - l^2]^3 \quad [7]$$

and the coupling matrix elements are given by

$$W_{20} = W_{02} = W_{-20} = W_{0-2} = q_v [J^2(J+1)^2 - 2J(J+1)]^{1/2} / \sqrt{2}$$

and

$$W_{2-2} = W_{-22} = \frac{1}{2} \rho_v [J^2(J+1)^2 - 2J(J+1)].$$

Because of its symmetry, Eq. [6] can be transformed into a 2×2 matrix representing the e levels,

$$E = \begin{vmatrix} E(X2^2Y) + W_{22} & \sqrt{2}W_{20} \\ \sqrt{2}W_{20} & E(X2^0Y) \end{vmatrix}, \quad [8]$$

and a 1×1 matrix representing the f levels,

$$E(X2^2Y) - W_{22}.$$

Even without that transformation, the eigenvectors of Eq. [6] show that there is no mixing of the 02^0 level with one of the two 02^2 levels, the f level. Consequently, l -type resonance does not mix the $l = 0$ state with the f level of the $l = 2$ state. This leaves unchanged the selection rule $\Delta l \neq 2$ for the f levels. Both e levels that are the eigenvalues

TABLE 2
 Measured Intensities ($10^{-4} \text{ cm}^{-2} \text{ atm}^{-1}$) of the $02^2_0-00^0_0$ Transitions for $\text{H}^{12}\text{C}^{14}\text{N}$ and $\text{H}^{12}\text{C}^{15}\text{N}$

J''	$\text{H}^{12}\text{C}^{14}\text{N}$ (at 296.5 K)						$\text{H}^{12}\text{C}^{15}\text{N}$ (at 297.2 K)						J''
	P-branch	(O-C)	R-branch	(O-C)	Q-branch	(O-C)	P-branch	(O-C)	R-branch	(O-C)	Q-branch	(O-C)	
5	0.22(8) ^a	0.17	1.49(5)	-0.40	0.61(3)	-0.26							5
6	4.81(8)	0.27					3.33(8)	-0.35			1.13(5)	-0.02	6
7	8.34(9)	-0.47	7.96(19)	-0.32	2.01(7)	0.11	6.44(8)	-0.66					7
8	13.57(21)	-1.52	13.92(18)	-0.18	2.52(6)	0.03	12.92(72)	0.79			2.28(6)	0.16	8
9	22.46(28)	-1.06			2.91(5)	-0.15							9
10	32.64(24)	-1.28	29.99(37)	-1.37	3.54(6)	-0.06	28.89(18)	1.66	24.46(54)	1.59			10
11	44.45(25)	-1.40	40.73(26)	-1.44	4.06(6)	0.00	35.00(59)	-1.84	32.41(54)	1.30			11
12	56.73(36)	-1.87	53.52(25)	-0.08	4.69(5)	0.29	47.69(53)	0.52	41.11(46)	1.11			12
13	70.97(36)	-0.30	63.37(28)	-1.45	4.55(6)	-0.05	57.27(53)	-0.26	49.00(43)	0.10	3.86(5)	-0.03	13
14	82.51(36)	-0.44	74.47(37)	-0.53	4.70(5)	0.03	68.78(63)	1.60	56.66(59)	-0.52			14
15	91.41(46)	-1.32	83.78(49)	0.45	4.39(7)	-0.21	74.65(78)	-0.77	63.28(73)	-0.91			15
16	102.00(48)	2.08	88.95(47)	-0.24			81.36(80)	-0.28	69.82(103)	0.39			16
17	105.79(47)	1.76	93.57(52)	1.35	4.05(5)	-0.08			72.00(83)	-0.55			17
18	106.45(79)	1.57	94.78(40)	2.47	3.90(5)	0.13	85.08(81)	-1.59	72.75(75)	-0.66			18
19	104.92(50)	2.33			3.46(5)	0.10	84.88(87)	-0.44	72.85(71)	0.81			19
20			85.77(41)	1.29					69.98(85)	1.30	2.43(3)	0.00	20
21	91.68(51)	1.54	79.04(40)	1.59			75.84(92)	-0.22	62.63(58)	-1.06	1.99(3)	-0.07	21
22			70.49(37)	1.36			68.74(80)	-0.30	57.50(60)	-0.02			22
23			96.11(32)	0.99	1.76(4)	0.04	62.80(83)	1.68	50.46(57)	-0.17	1.42(3)	0.02	23
24	63.58(30)	2.53	51.73(30)	0.75	1.50(4)	0.12	56.28(63)	3.45			1.21(3)	0.09	24
25	52.98(43)	1.92			1.11(4)	0.03	44.21(51)	-0.39	34.93(53)	-1.52			25
26			33.66(22)	-0.44	0.59(3)	-0.25			29.31(46)	-0.53			26
27							29.93(48)	0.23	24.00(36)	0.12			27
28	26.17(24)	0.13	22.26(25)	1.48			23.37(44)	-0.09	17.41(27)	-1.28			28
29	19.72(20)	-0.20	14.99(18)	-0.68			18.36(32)	0.22	14.15(33)	-0.15			29
30	14.66(20)	-0.25	11.48(18)	-0.09			13.91(11)	0.18	10.57(29)	-0.14			30
31	9.61(20)	-1.31	8.31(16)	-0.04			9.81(11)	-0.38	7.62(30)	-0.23			31
32	6.78(22)	-1.06	5.72(4)	-0.18			7.41(8)	0.02	7.18(29)	1.55			32
33			3.85(4)	-0.23			7.06(26)	1.79	5.25(17)	1.29			33
34			2.65(5)	-1.09					3.46(12)	0.74			34
35	2.19(5)	-0.38					3.99(11)	1.47	2.78(11)	0.95			35
36	1.23(4)	-0.47							1.75(7)	0.54			36

^a The uncertainty in the last digits (one standard deviation given by the fit of the line shape) is given in parentheses.

for Eq. [8] are really a mixture of $l = 0$ and $l = 2$ states, consequently the selection rule $\Delta l = 0$ can be applied to transitions from the ground state to either of the two e states.

To use the best form for Eq. [3] to represent the effect of l -type resonance we need to know the approximate form of the mixing coefficient given by the energy matrix, Eq. [8]. The perturbed form of the wavefunction for the 02^2_0 level may be given by

$$\psi(02^2_0) = a\psi^0(02^2_0) - b\psi^0(02^0_0),$$

where

$$a^2 + b^2 = 1$$

and

$$b^2 = \frac{1}{2}[(1 + X)^{1/2} - 1](1 + X)^{-1/2} \quad [9]$$

with

$$X = 8W_{20}^2/[E(02^2_0) + W_{22} - E(02^0_0)]^2.$$

Expanding Eq. [9] in a power series, retaining only the first terms, and leaving out the W_{22} term because it is so small gives

$$b = \frac{1}{2}X^{1/2} = q_v[J^2(J+1)^2 - 2J(J+1)]^{1/2}/[E(02^2_0) - E(02^0_0)].$$

Thus the dominant term in the transition dipole moment for the $02^2_0-00^0_0$ transitions will be

$$\begin{aligned} CF(J) &= bR(02^0_0-00^0_0) \\ &= q_vR(02^0_0-00^0_0)[J^2(J+1)^2 - 2J(J+1)]^{1/2}/[E(02^2_0) - E(02^0_0)], \end{aligned} \quad [10]$$

TABLE 3
Measured Intensities ($10^{-6} \text{ cm}^{-2} \text{ atm}^{-1}$) of the 12^20-00^00 and 02^21-00^00 Transitions of HCN

J''	12^20-00^00 (at 298.6 K)						02^21-00^00 (at 298.0 K)							
	P-branch (O-C)		R-branch (O-C)		Q-branch (O-C)		P-branch (O-C)		R-branch (O-C)		Q-branch (O-C)		J''	
5														5
6									10.98(30) ^a	-0.09			6	
7									20.37(44)	0.99			7	
8									30.17(35)	-0.75			8	
9									43.99(20)	-1.70			8	
10				2.47(7)	-0.27			12.53(18)	-0.16	80.89(33)	-2.13	4.29(14)	0.16	9
11				4.01(6)	0.16			17.37(17)	-1.49			4.80(23)	-0.06	10
12	4.83(33)	-0.96				1.33(5)	-0.26	24.70(14)	-1.37	123.09(64)	-0.63	6.27(14)	0.33	12
13				6.38(7)	0.02	1.63(7)	0.01	33.14(17)	-0.70	143.35(29)	1.43			13
14	6.56(29)	-1.23		7.52(8)	-0.08	1.58(4)	-0.02	43.66(64)	2.04	157.08(46)	0.21	5.55(21)	-0.78	14
15				8.57(8)	-0.12	1.95(6)	0.42	48.45(17)	-0.31	164.61(47)	-2.94			15
16				9.87(10)	0.30	1.27(7)	-0.15	54.64(17)	-0.06			5.87(20)	-0.14	16
17				10.75(12)	0.60			59.53(21)	0.55	175.76(40)	1.99	6.23(12)	0.60	17
18				10.61(12)	0.18	1.20(3)	0.06	62.89(16)	1.58	172.33(37)	3.03			18
19				10.27(18)	-0.10	0.72(8)	-0.26	61.44(34)	-0.16			4.07(17)	-0.53	19
20	8.06(10)	0.15		10.62(12)	0.61	0.85(4)	0.02			145.48(134)	-2.54	3.51(17)	-0.51	20
21	7.62(17)	0.48		9.69(15)	0.29					137.40(78)	4.29			21
22	6.97(20)	0.71		8.30(13)	-0.29			52.83(15)	0.94	117.69(37)	0.95	2.56(11)	-0.33	22
23	5.80(15)	0.44		7.31(13)	-0.34			46.42(15)	0.12	97.31(49)	-2.63			23
24	4.10(16)	-0.36		6.49(10)	-0.15					81.74(50)	-1.81			24
25	2.91(6)	-0.71		5.78(14)	0.15			33.98(16)	-0.08	64.49(69)	-3.78			25
26	2.94(6)	0.06		4.71(10)	0.05			27.63(14)	-0.51	56.33(69)	1.82			26
27	2.41(6)	0.18		3.76(13)	-0.01			17.72(33)	-4.98	38.32(51)	-4.25			27
28				2.51(10)	-0.47			17.59(12)	-0.29	32.57(60)	0.04			28
29				2.21(3)	-0.10					22.50(51)	-1.83			29
30				1.74(4)	-0.01			9.39(23)	-0.97	15.08(60)	-2.72			30

^a The uncertainty in the last digits (one standard deviation given by the fit of the line shape) is given in parentheses.

or

$$C = q_v R(02^00-00^00)/[E(02^20) - E(02^00)], \quad [11]$$

and

$$F(J) = [J^2(J+1)^2 - 2J(J+1)]^{1/2}, \quad [12]$$

where $J = J'$ because the upper state is the one that is involved in the resonance. The J -dependence of Eq. [12] is the same as that for the C_3 term of Eq. [4]. Since this is based on the transition dipole $R(02^00-00^00)$, then the Hönl-London term, L_2 in Eq. [4], must be the one appropriate for a $\Delta l = 0, l = 0$ transition. Obviously, equations similar to Eq. [11] could be derived for any $v_2 = 2$ state. The values of C given by appropriate variations of Eq. [11] are listed in the last column of Table 5 and should be compared with the values of C_3 in that table. In addition to the C_3 term in Eq. [4], we have added a C_4 term that has an additional $J(J+1)$ dependence in order to allow for higher order terms that were ignored in our derivation of Eq. [10].

To see how well Eq. [11] agrees with a more detailed

calculation and also to compare the expected intensity pattern with what is observed, we have calculated the intensity of all the lines for the P and R branches of the bands measured in this work using the eigenvectors given by the diagonalization of the energy matrix. All of the constants needed to evaluate the energy matrix, Eq. [6], have been given by Maki *et al.* (7, 8) so it was easy to calculate exactly the effect of the resonance in transferring intensity from the $X 2^0Y-00^00$ transitions to the $X 2^2eY-00^00$ transitions. More details of that calculation have been given by Maki *et al.* (2) who followed the formulation given by DiLauro and Mills (12). These calculations used the transition dipoles given in Table 1.

The calculated intensities were fitted in the same way that the experimental intensity values were fitted and the resulting constants are given in the rows labeled "calc." in Table 5. Those rows do not give any value for C_1 because it was in all cases an order of magnitude smaller than the observed value and smaller than its uncertainty. To have a realistic comparison between the constants given by the calculated and observed intensities, the fit of the calculated transition intensities included only those transitions whose intensity was measured and the weight given to each mea-

TABLE 4
Measured Intensities ($10^{-4} \text{ cm}^{-2} \text{ atm}^{-1}$) of the 02^20-00^00 Transitions for $\text{D}^{12}\text{C}^{14}\text{N}$ and $\text{D}^{13}\text{C}^{15}\text{N}$

$\text{D}^{12}\text{C}^{14}\text{N}$ (at 297.7 K)							$\text{D}^{13}\text{C}^{15}\text{N}$ (at 296.5 K)					
J''	<i>P</i> -branch (O-C)		<i>R</i> -branch (O-C)		<i>Q</i> -branch (O-C)		<i>P</i> -branch (O-C)	<i>R</i> -branch (O-C)		<i>Q</i> -branch (O-C)		J''
8			7.01(30) ^a	-0.34					4.16(23)	-0.29		8
9			10.90(40)	-0.34			4.13(21)	-0.45	6.44(16)	-0.34		9
10	7.05(42)	-5.18	16.40(40)	0.37			6.35(22)	-0.53	9.27(17)	-0.42		10
11	15.60(50)	-1.44	21.00(40)	-0.57					12.42(17)	-0.65		11
12	23.30(60)	0.86	28.20(40)	0.63	0.42(14)	0.25			18.97(26)	2.20		12
13	36.40(60)	8.26	33.90(40)	0.23	0.11(4)	-0.08	15.87(17)	-0.49	20.11(23)	-0.48		13
14			39.00(60)	-0.46			19.81(20)	-0.07				14
15	36.8(40)	-2.16	44.50(40)	-0.03			22.94(18)	-0.28	28.09(16)	0.49		15
16	41.6(40)	-1.75	49.20(40)	0.67	0.86(13)	0.65	26.58(18)	0.42	31.97(17)	1.63	9.27(168)	1.56
17			51.10(40)	-0.10			28.99(17)	0.46	32.36(16)	0.05	5.13(121)	-2.50
18	53.90(40)	5.27	52.40(40)	0.02			29.76(21)	-0.41	33.45(16)	0.05	8.71(154)	1.34
19	48.90(40)	-0.32	52.20(40)	0.16			31.14(13)	0.15	33.12(15)	-0.44	6.99(98)	0.00
20	46.70(50)	-1.74	51.10(40)	0.82			31.35(15)	0.38	32.48(15)	-0.35		20
21			47.00(40)	-0.28	0.12(8)	-0.03			31.45(19)	0.15		21
22			42.00(30)	-1.30			28.47(16)	-0.18	28.26(14)	-0.82		22
23	38.10(60)	-1.35	38.60(30)	-0.06			26.67(16)	0.11	25.89(14)	-0.48		23
24	34.60(30)	-0.46	34.80(40)	1.14					22.70(16)	-0.65	5.36(107)	1.28
25	30.40(30)	-0.02	27.00(40)	-1.59			21.47(14)	0.17	20.14(14)	-0.05		25
26	25.60(30)	-0.19	23.70(30)	0.02			18.36(13)	-0.08	18.38(16)	1.33		26
27	21.70(30)	0.33	19.40(30)	0.26			15.49(11)	-0.12	13.60(16)	-0.48		27
28							12.71(10)	-0.23	11.67(11)	0.32		28
29	14.10(20)	0.41	11.80(30)	0.20			10.54(11)	0.04	9.00(13)	0.06		29
30	9.67(27)	-0.93	10.30(50)	1.61			8.28(11)	-0.07	7.40(14)	0.52		30
31	7.56(18)	-0.46							5.24(12)	0.08		31
32	6.17(21)	0.25	6.18(30)	1.68			4.85(10)	-0.10				32
33	4.97(26)	0.69					3.61(9)	-0.08	3.14(13)	0.44		33
34							2.55(9)	-0.14	2.32(12)	0.44		34
35									1.63(12)	0.37		35
36							1.59(8)	0.25	1.19(16)	0.36		36
37							1.00(9)	0.09				37

^a The uncertainty in the last digits (one standard deviation given by the fit of the line shape) is given in parentheses.

surement was also attached to each of the calculated intensities. This was done for each of the bands given in Table 5 and the agreement between the calculated and so-called observed constants for the $e-e$ transitions was very pleasing.

However, when we fit the measured intensities of the forbidden P - and R -branch transitions with only the constants C_3 and C_4 the residuals of the fit were very large and were systematically of opposite sign in the P branch from the residuals in the R branch. It was obvious that some constant was needed which would have a sign that depended on the sign of $J'-J''$. The next section shows that the constants needed to improve the fit of the P - and R -branch intensities are the same constants needed to fit the intensities of the Q -branch transitions.

Intensity Contribution from Other Coriolis Sources

As shown above, l -type resonance does not affect the intensity of the Q -branch transitions of the type $X2^2fY-00^00$. In addition, l -type resonance cannot explain the ob-

served asymmetry of the P - and R -branch intensities, i.e., the C_1 constants. If we assume that there is no way to mix the e and f levels, then the extra intensity factors must come from some Coriolis interaction between the upper and or lower states and an $l = 1$ state because that is the only type of state to which both upper and lower states can make allowed $\Delta J = 0$ transitions. It would serve no purpose to investigate an interaction that does not lead to an allowed transition, such as a purely vibrational interaction.

For a weak $\Delta l = \pm 1$ Coriolis interaction affecting the upper state the energy matrix will have the form

$$E = \begin{vmatrix} E(X2^2fY) & W_{12} \\ W_{12} & E(\text{perturber}) \end{vmatrix}, \quad [13]$$

where

$$W_{12} = z\{J(J+1) - 2\}^{1/2}$$

which is the correct J -dependence for a $\Delta l = \pm 1$ perturbation. Treating the energy matrix, Eq. [13], in the same way as Eq. [8] above we find that the contribution of this Coriolis interaction to the intensity of the $X 2^2fY - 00^00$ transition will be

$$CF(J) = bR(\text{perturber}-00^00) \\ = zR(\text{perturber}-00^00)[J'(J' + 1) - 2]^{1/2} \\ / [E(X 2^2fY) - E(\text{perturber})],$$

or

$$z = C_1 [E(X 2^2fY) - E(\text{perturber})] \\ / R(\text{perturber}-00^00), \quad [14]$$

where $R(\text{perturber}-00^00)$ is the transition dipole moment for the transition from the ground state to the perturber state. In these equations we have used z to represent the Coriolis interaction constant. In some cases the Coriolis interaction constant is represented by a term such as $z = 2B\zeta$ where ζ usually has a value between ± 1 and 0 (12).

Since the perturbing state cannot be an $l = 0$ state, it is evident that a nearly identical matrix must also apply to the $X 2^2eY$ levels and so the same intensity perturbation should be found for the P - and R -branch transitions. This accounts for the C_1 term in Eq. [4]. The L_1 term will be a Hönl-London term for perpendicular transitions such as 01^10-00^00 . It is convenient that the L_1 term that applies to P - and R -branch transitions (Eq. [5]) has a term $(J' - J'')$ that is negative for P -branch transitions and positive for R -branch transitions. Certain conventions could reverse these signs. Similar arguments could be made for a Coriolis interaction involving the lower, ground, state.

We have also added to Eq. [4] an extra term, C_2 , that is intended to allow for higher order terms left out of our derivation. The C_2 term was included in the fits of P - and R -branch intensities but the uncertainty indicates it may not be significant in most cases.

This explanation requires that the C_1 term have the same value for the Q -branch transitions and for the P - and R -branch transitions. Table 5 shows that the fits of the observed intensities do fulfill this requirement. The relative sign of the transition dipole, the C_1 term, cannot be determined from the Q -branch measurements, but the magnitude is in good agreement with the same term for the P - and R -branch transitions.

Intensity Contribution from l -Type Resonance for $v_2 = 3$

The case of $X 3^3Y - 00^00$ transitions is different from the $\Delta v_2 = 2$ transitions because both the e and f levels of the $l = 3$ state undergo a mixing with the $l = 1$ state. For the

particular case of the $03^{1\&3}0$ levels the energy matrix has the form

$$E = \begin{vmatrix} E(03^30) & W_{31} & W_{3-1} & 0 \\ W_{13} & E(03^10) & W_{1-1} & W_{1-3} \\ W_{-13} & W_{-11} & E(03^{-1}0) & W_{-1-3} \\ 0 & W_{-31} & W_{-3-1} & E(03^{-3}0) \end{vmatrix}, \quad [15]$$

where

$$W_{31} = W_{13} = W_{-1-3} = W_{-3-1} \\ = \sqrt{3}q[J^2(J+1)^2 - 8J(J+1) + 12]^{1/2}/2, \\ W_{1-1} = W_{-11} = qJ(J+1), \\ W_{3-1} = W_{-13} = W_{-31} = W_{1-3} \\ = \sqrt{3}\rho J(J+1)[J^2(J+1)^2 \\ - 8J(J+1) + 12]^{1/2}/2,$$

and the energy levels are given by Eq. [7].

Equation [15] can be further simplified by transforming to two 2×2 matrices in the form

$$E = \begin{vmatrix} E(03^30) & (W_{31} \pm W_{3-1}) \\ (W_{31} \pm W_{3-1}) & E(03^10) \pm W_{1-1} \end{vmatrix}, \quad [16]$$

where the matrix with the upper sign applies to the f levels and the one with the lower sign applies to the e levels. This has the same form as Eq. [8] so that the contribution to the transition dipole moment will be given by

$$CF(J) = \sqrt{3}qR(03^10-00^00)[J^2(J+1)^2 \\ - 8J(J+1) + 12]^{1/2} \\ / 2[E(03^30) - E(03^10) \mp W_{1-1}]. \quad [17]$$

This has a slightly different J -dependence from what is in Eq. [4] so we have fit the data for the forbidden $\Delta l = 3$ transitions to the following revision of Eq. [4]:

$$R = L_2 \{ C_3 + C_4 J'(J' + 1) \} \{ J'^2(J' + 1)^2 \\ - 8J'(J' + 1) + 12 \}^{1/2}. \quad [18]$$

In Eq. [18] the Hönl-London term L_2 will be the same as the L_1 term in Eq. [4] in order to be appropriate for the $\Delta J = 0$ or ± 1 transitions for 03^10-00^00 because those transitions are assumed to provide most of the transition dipole for the 03^30-00^00 transitions. The first set of deviations shown in Table 6, $(O - C_1)$, came from a least-squares fit of the measured intensities of all the $\Delta l = 3$ transitions to Eq. [18].

TABLE 5
Components of the Transition Dipole Moment Arising from a $\Delta l = \pm 1$ Coriolis Interaction and l -type Resonance (the Signs Are Relative to a Positive C_3)

transition	C_1 (debye)	C_2 (debye)	C_3 (debye)	C_4 (debye)	C_5 Eq. [11](debye)
HCN					
obs. $02^2_0-00^0_0$	$-8.5(3)^a \times 10^{-5}$	$-0.1(10) \times 10^{-8}$	
obs. $02^{2e}_0-00^0_0$	$-8.4(4) \times 10^{-5}$	$-5.1(14) \times 10^{-8}$	$2.58(2) \times 10^{-5}$	$-5.9(4) \times 10^{-9}$	
calc. ^b $02^{2e}_0-00^0_0$	$2.62(2) \times 10^{-5}$	$-6.5(4) \times 10^{-9}$	2.5×10^{-5}
obs. $12^2_0-00^0_0$	$-2.7(2) \times 10^{-6}$	
obs. $12^{2e}_0-00^0_0$	$-2.2(4) \times 10^{-6}$	$4.0(8) \times 10^{-9}$	$4.39(15) \times 10^{-7}$	$-1.2(3) \times 10^{-10}$	
calc. $12^{2e}_0-00^0_0$	$4.32(3) \times 10^{-7}$	$-1.0(1) \times 10^{-10}$	4.1×10^{-7}
obs. $02^2_1-00^0_0$	$6.3(2) \times 10^{-6}$	
obs. $02^{2e}_1-00^0_0$	$6.2(3) \times 10^{-6}$	$-2.6(10) \times 10^{-9}$	$1.69(2) \times 10^{-6}$	$-4.3(4) \times 10^{-10}$	
calc. $02^{2e}_1-00^0_0$	$1.78(1) \times 10^{-6}$	$-3.8(2) \times 10^{-10}$	1.7×10^{-6}
HC ¹⁵ N					
obs. $02^2_0-00^0_0$	$-8.1(3) \times 10^{-5}$	$-1.3(6) \times 10^{-8}$	
obs. $02^{2e}_0-00^0_0$	$-8.3(6) \times 10^{-5}$	$-3.3(14) \times 10^{-8}$	$2.29(3) \times 10^{-5}$	$-5.3(5) \times 10^{-9}$	
calc. $02^{2e}_0-00^0_0$	$2.41(1) \times 10^{-5}$	$-5.2(3) \times 10^{-9}$	2.3×10^{-5}
obs. $02^2_1-00^0_0$	$6.9(12) \times 10^{-6}$	
obs. $02^{2e}_1-00^0_0$	$4.8(3) \times 10^{-6}$...	$1.70(3) \times 10^{-6}$	$-4.6(8) \times 10^{-10}$	
calc. $02^{2e}_1-00^0_0$	$1.77(1) \times 10^{-6}$	$-3.5(2) \times 10^{-10}$	1.8×10^{-6}
H ¹³ C ¹⁵ N					
obs. $02^2_1-00^0_0$	$3.6(12) \times 10^{-6}$	
obs. $02^{2e}_1-00^0_0$	$4.0(3) \times 10^{-6}$...	$1.93(3) \times 10^{-6}$	$-5.5(5) \times 10^{-10}$	
calc. $02^{2e}_1-00^0_0$	$1.84(1) \times 10^{-6}$	$-3.6(2) \times 10^{-10}$	1.8×10^{-6}
DCN					
obs. $02^2_0-00^0_0$	$-2.0(12) \times 10^{-5}$	
obs. $02^{2e}_0-00^0_0$	$-4.2(9) \times 10^{-5}$	$-1.6(20) \times 10^{-8}$	$2.06(4) \times 10^{-5}$	$-9.1(7) \times 10^{-9}$	
calc. $02^{2e}_0-00^0_0$	$1.99(1) \times 10^{-5}$	$-8.6(2) \times 10^{-9}$	1.9×10^{-5}
D ¹³ C ¹⁵ N					
obs. $02^2_0-00^0_0$	$-2.6(6) \times 10^{-5}$	
obs. $02^{2e}_0-00^0_0$	$-3.5(4) \times 10^{-5}$	$-2.8(10) \times 10^{-8}$	$2.04(2) \times 10^{-5}$	$-8.3(3) \times 10^{-9}$	
calc. $02^{2e}_0-00^0_0$	$1.89(1) \times 10^{-5}$	$-7.7(2) \times 10^{-9}$	1.8×10^{-5}

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

^b The calculated constants are based on a least-squares fit of the intensities given by a calculation of the l -type resonance mixing of the $l = 0$ and $l = 2$ levels (see text) except that the last column is based on Eq. [11].

The experimental intensity measurements are given in Table 6 and the constants that resulted from the least-squares fits of the data are given in Table 7. Table 7 also gives the constants that were determined by calculating the line intensities and fitting those calculated intensities to Eq. [18]. Those calculated intensities were based on the measured transition dipole moment given in Ref. (3) for the $03^1_0-00^0_0$ transition and took into account the mixing of the 03^1_0 and 03^3_0 levels through l -type resonance. This is the fit that gives the calculated values for the second set of deviations,

$(O - C_{II})$, shown in Table 6. Since that set of calculated intensities was not based on these measurements, it is not surprising that the sum of the deviations is negative rather than zero. In fact, it is surprising to us that the agreement is as good as it is.

DISCUSSION OF RESULTS

$\Delta l = 2$ Transitions

In interpreting the results given in Table 5 one should keep in mind several points. The constant C_2 was included

TABLE 6
Measured Intensities ($10^{-6} \text{ cm}^{-2} \text{ atm}^{-1}$ at 298.8 K) of the $03^3_0-00^0_0$ Transitions of $\text{H}^{12}\text{C}^{14}\text{N}$

J''	P -branch	$(\text{O}-C_1)^a$	$(\text{O}-C_{II})^b$	R -branch	$(\text{O}-C_I)$	$(\text{O}-C_{II})$	Q -branch	$(\text{O}-C_I)$	$(\text{O}-C_{II})$
8							1.44(12) ^c	-0.24	-0.38
9							2.21(8)	-0.47	-0.68
10				2.54(10)	-0.19	-0.66	3.47(8)	-0.48	-0.80
11				3.57(23)	0.05	-0.57	5.92(9)	0.44	0.02
12	1.66(8)	-0.09	-0.39	3.95(8)	-0.38	-1.15			
13				4.58(6)	-0.50	-1.43			
14				5.04(9)	-0.69	-1.77			
15				5.46(9)	-0.77	-1.98			
16				6.72(6)	0.17	-1.14			
17	3.81(8)	0.30	-0.38	6.73(10)	0.07	-1.30	14.97(7)	-0.13	-1.02
18	5.08(22)	1.50	0.78	5.89(12)	-0.68	-2.08	16.89(11)	1.05	0.18
19				5.96(8)	-0.33	-1.72			
20				6.68(5)	0.82	-0.53			
21	4.74(8)	1.58	0.88	5.02(4)	-0.30	-1.56	15.29(7)	-0.23	-0.87
22	5.17(7)	2.31	1.65	4.73(6)	0.03	-1.13			
23	4.32(11)	1.80	1.20	3.66(4)	-0.39	-1.44			
24	3.43(9)	1.27	0.73	2.93(6)	-0.47	-1.40	11.73(5)	-0.48	-0.75
25				2.76(6)	-0.04	-0.83	10.70(5)	-0.08	-0.23
26	2.29(5)	0.81	0.41	1.95(3)	-0.29	-0.97			
27				1.48(9)	-0.28	-0.84	8.94(4)	1.05	1.10
28				1.46(5)	0.11	-0.34	6.03(7)	-0.51	-0.40
29							4.77(8)	-0.55	-0.39
31							2.84(4)	-0.48	-0.28
32							2.61(5)	0.06	0.26
33							1.59(4)	-0.34	-0.14

^a The first set of Obs.-Calc. were based on the least-squares fit of the measured intensities to Eq. [18].

^b The second set of Obs.-Calc. were based on measured intensities minus the values calculated for the l -type resonance mixing of the $l=1$ and $l=3$ levels.

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

in the fits for the sake of completeness but in no case does there seem to be a significant value determined for that constant. In only two cases were enough Q -branch transitions measured to warrant including the C_2 term in the fit and in both those cases the term was not significant. Until more accurate intensity values become available, the C_2 constants should be considered to be experimental artifacts. The residuals of the least-squares fits are not noticeably worse in fits that leave out the C_2 constants.

In four cases, the $02^{2f}0-00^0_0$ transitions of DCN and $\text{D}^{13}\text{C}^{15}\text{N}$ and the $02^{2f}1-00^0_0$ transitions of $\text{H}^{12}\text{C}^{15}\text{N}$ and $\text{H}^{13}\text{C}^{15}\text{N}$, the signal-to-noise ratio for the measurements of the forbidden Q -branch transitions is so poor ($S/N \approx 2$) that the measurements for C_1 given in Table 5 are only reliable as an estimate of the correct order of magnitude. The values for C_1 given by the fits of the P - and R -branch transitions are much more reliable. Ralf Petry has also made

TABLE 7
Constants from the Least-Squares Fits of the Measured and Calculated Intensities to Eq. [18]

transition	C_3 (debye) $\times 10^6$	C_4 (debye) $\times 10^9$
obs. $03^3_0-00^0_0$	0.69(4) ^a	0.24(8)
calc. ^b $03^3_0-00^0_0$	0.730(6)	0.183(10)
obs. $03^3_e0-00^0_0$	0.67(6)	-0.19(12)
calc. $03^3_e0-00^0_0$	0.718(1)	-0.155(1)

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

^b The calculated constants are based on a least-squares fit of the intensities given by a calculation of the l -type resonance mixing of the $l=1$ and $l=3$ levels (see text).

diode laser measurements of the Q -branch lines for DCN and $D^{13}C^{15}N$ with a $S/N = 10$ or better, but for other reasons intensity measurements were not possible (9).

As indicated before, the sign of the C_1 constant is not obtainable from the Q -branch measurements. In Table 5 the signs of all the constants are taken from the fits of the intensities for the P - and R -branch transitions and are all based on an assumed positive sign for the C_3 constant. The data are fit equally well when the signs of all constants are reversed. The signs of the constants are also dependent on the signs used for the Hönl–London terms.

There is very good agreement between the observed and calculated values of the C_3 and C_4 constants as shown in Table 5. In making the fits of the calculated intensities for the $X2^eY-00^0$ transitions we also tried to determine values for the C_1 and C_2 constants and in all cases they were close to zero with uncertainties larger than the values. This is strong evidence that the C_3 and C_4 terms are almost entirely due to the effects of l -type resonance and the C_1 and C_2 terms must come from some other source.

The agreement between the values of the C_1 terms observed for both the $\Delta J = 0, f-e$ transitions and the $\Delta J = \pm 1, e-e$ transitions indicates that the same interaction, or combination of interactions, affects both the e and f levels for $l = 2$. That interaction would have to be with a level with $l > 0$ in order to affect both the e and f levels. The relative signs of C_1 and C_3 are the same for all isotopic species but are not the same for all transitions. C_1 has the same sign as C_3 for the 02^21-00^0 transitions but the opposite sign for the other two. C_1 is large enough for its sign to be apparent just from a quick look at the spectrum because the R branch is at least twice as strong as the P branch if C_1 is positive and the R branch is less than twice as strong as the P branch if C_1 is negative, with respect to a positive C_3 . This is easily seen in Tables 2, 3, and 4.

All the evidence points to the validity of the assumption that the value of C_1 comes from some Coriolis interaction that mixes either or both the upper and lower states with l states such that the transition has the character of a $\Delta l = \pm 1$ transition. In Fig. 4 we show all the energy levels of f parity, or symmetry, below 4900 cm^{-1} . Each of these levels could, in principle, interact with the upper state of the $\Delta l = 2, f-e$ transitions. Each of the levels shown in Fig. 4 is accompanied by an e level which would interact with the upper state e levels through the same interaction constant. The e levels also could interact with the lower state, the ground state, but the f levels could not.

Since this paper is concerned with transitions from the ground state, let us look first at the possibilities for interactions that might affect the mixing of the ground state with $l = 1$ states. If the values of the C_1 constants are only due to interactions with the lower, ground state, then the values of C_1 will be proportional to the transition dipole moments for transitions from the same perturbing state to the appro-

priate upper state. The most likely possibility is that the ground state is mixed with the 01^10 state which is the closest $l = 1$ state. For the various cases, this would mean that

$$\begin{aligned} & |C_1(02^20-00^0)/R(02^20-01^10)| \\ &= |C_1(12^20-00^0)/R(12^20-01^10)| \quad [19] \\ &= |C_1(02^21-00^0)/R(02^21-01^10)|. \end{aligned}$$

To evaluate these ratios we have assumed that the value for $R(12^20-01^10)$ is the same as $R(11^10-00^0)$ which according to Ref. (3) seems to be a good assumption, to within about 8%. The same assumption was applied to $R(02^21-01^10)$ and $R(01^11-00^0)$. While the above ratios are the same order of magnitude, they are not the same; they vary from 0.00022 to 0.00075. This makes it seem unlikely that some ground state coupling is the sole source of the observed intensity. There will also be weak couplings between the ground state and other $l = 1$ states but there is no reason to expect they will be any stronger and since they are more distant they would probably be less significant.

To simplify the discussion of possibilities for upper state mixing, we can consider the simplest example, the $02^{2f}0-00^0$ transitions. The nearest $l = 1$ levels that might interact with the 02^20 level are 01^10 , 03^10 , 01^11 , and 11^10 , none of which is closer than 680 cm^{-1} . The transition dipole moments between the ground state and these upper states are given in Table 1.

Because the transition dipole to the 01^10 state is 50 times greater than the transition dipole to the 03^10 state and because they should have the same Coriolis coupling constant with the 02^20 state, it is unlikely that a mixing with the 03^10 state could contribute much to the intensity. We can estimate the contributions of the 01^11 and 11^10 levels to the intensity of the $02^{2f}0-00^0$ transitions because we have values for $\zeta_{23} = 0.153$ and $\zeta_{12} = 0.988$ given by Nakagawa and Morino (13). The Coriolis coupling term, z , is usually given by $2B\zeta$ and the other constants in Eq. [14] are known so we can estimate that the contribution to C_1 will be $1.0 \times 10^{-5} \text{ D}$ from the 11^10 interaction and $0.2 \times 10^{-5} \text{ D}$ from the 01^11 interaction. These estimates may be in error by a factor of 2 and there is no guarantee that they will add together rather than subtract, but even so these interactions do not seem to be able to explain all the observed intensity.

If all of the intensity for $02^{2f}0-00^0$ comes from the $01^{1f}0-00^0$ transition, then the interaction term, z , must be given by Eq. [14] and is about 0.32 cm^{-1} which gives a ζ of about 0.1. This same interaction also would have to apply to the ground state and so its effect would either cancel or be doubled. Based on these considerations, it seems most likely that the intensity of the $02^{2f}0-00^0$ transitions comes in part from a Coriolis interaction of the upper state (02^20) with the 01^10 state and also from the same interaction be-

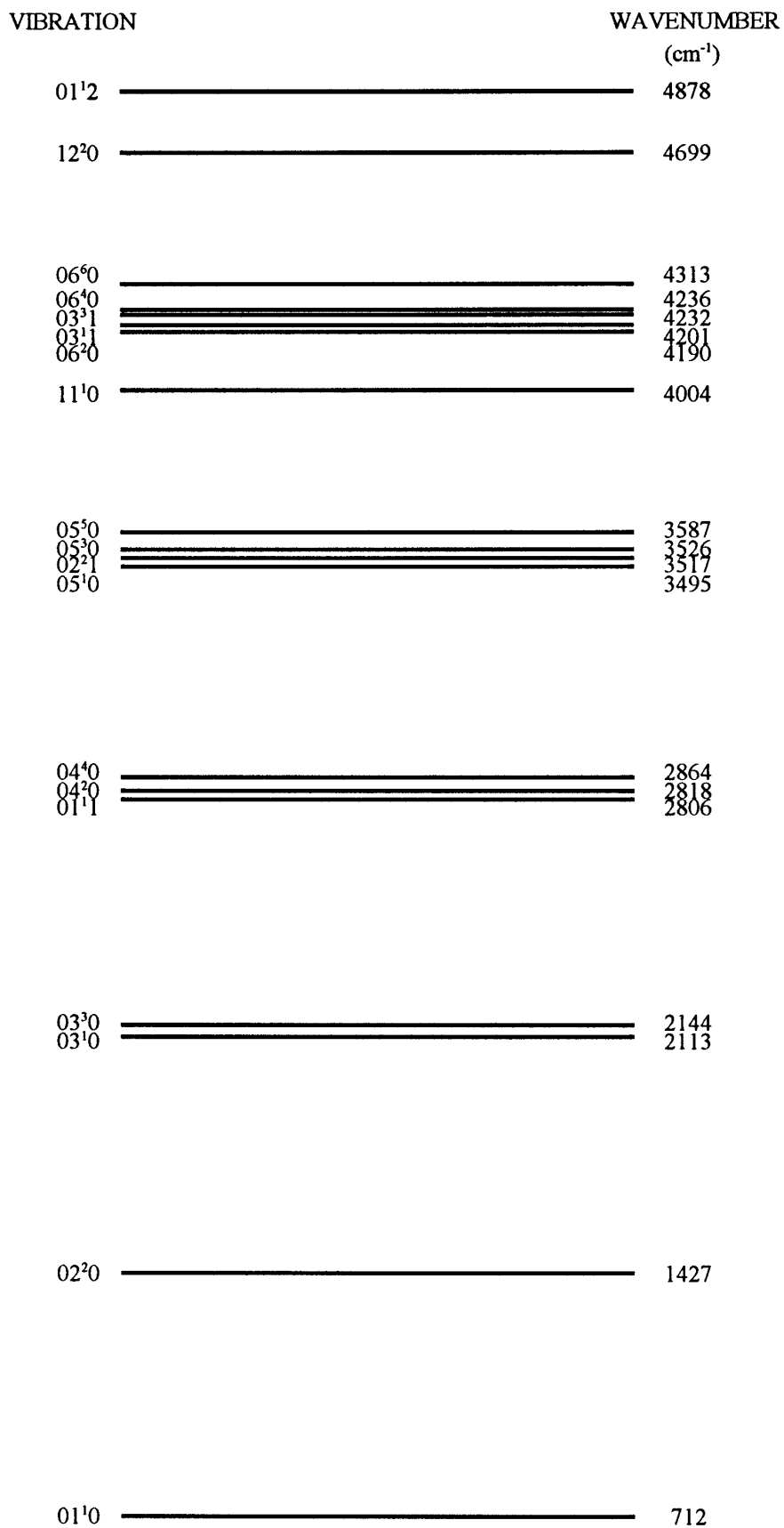


FIG. 4. All of the energy levels of f symmetry for HCN below 4900 cm^{-1} . In this diagram the wavenumber scale is based on zero wavenumbers for the ground vibrational state.

tween the ground state and the 01^1_0 state. There also will be contributions from interactions with the 01^1_1 and 11^1_0 states.

There are even more candidates for the perturbing level for the higher states but probably the same interactions are responsible for the majority of the intensity. Otherwise we might expect a greater variation in the size of the ratios given by Eq. [19]. If that is the case then much of the intensity of the $02^{2f}1-00^0_0$ transitions may come from the $01^{1f}1-00^0_0$ and $02^{2f}1-01^{1e}0$ transitions and similarly the $12^{2f}0-00^0_0$ transition intensity may come largely from the $11^{1f}0-00^0_0$ and $12^{2f}0-01^{1e}0$ transitions.

The smaller value of C_1 for the deuterated isotopomer was surprising because the energy levels are closer together. It must be due in part to a smaller Coriolis coupling constant and in part to the weaker transition dipoles for those transitions contributing to the C_1 term (see Table 1).

$\Delta l = 3$ Transitions

As can be seen in Tables 6 and 7, the agreement between the observed and calculated transition intensities and constants shows that most of the intensity of these transitions comes from l -type resonance. There is still a small discrepancy, especially noticeable in the R branch, that is probably an indication that some other Coriolis interactions are contributing to the intensity. In this regard one should particularly note the column of $(O - C_{II})$ in Table 6.

We would expect that the same Coriolis matrix elements that affect the 02^2_0 state would also affect the 03^3_0 state although they would connect the 03^3_0 state with energy levels that have one more quantum of ν_2 than the levels that affect the 02^2_0 state. In addition, there may be other Coriolis interactions affecting the 03^3_0 state.

It is not surprising that l -type resonance seems to account for most of the intensity of the $\Delta l = 3$ transitions because a single $\Delta l \pm 1$ Coriolis interaction could not contribute any intensity. Instead, either two $\Delta l \pm 1$ Coriolis interactions are needed or one $\Delta l \pm 2$ interaction.

ACKNOWLEDGMENTS

We are indebted to Dr. John Johns for making his INTBAT computer program available. A.M. and W.Q. also thank Drs. Brenda and Manfred Winnewisser for their hospitality and help in making the facilities in Giessen available to us.

REFERENCES

1. A. Maki, W. Quapp, S. Klee, G. C. Mellau, and S. Albert, *J. Mol. Spectrosc.* **174**, 365–378 (1995).
2. A. G. Maki, W. B. Olson, and R. L. Sams, *J. Mol. Spectrosc.* **36**, 433–447 (1970).
3. A. Maki, W. Quapp, and S. Klee, *J. Mol. Spectrosc.* **171**, 420–434 (1995).
4. D. Romanini and K. K. Lehmann, *J. Chem. Phys.* **102**, 633–642 (1995).
5. J. M. Brown, J. T. Hougen, K.-P. Huber, J. W. C. Johns, I. Kopp, H. Lefebvre-Brion, A. J. Merer, D. A. Ramsay, J. Rostas, and R. N. Zare, *J. Mol. Spectrosc.* **55**, 500–503 (1975).
6. J.-I. Choe, D. K. Kwak, and S. G. Kukolich, *J. Mol. Spectrosc.* **121**, 75–83 (1987).
7. A. Maki, W. Quapp, S. Klee, G. C. Mellau, and S. Albert, *J. Mol. Spectrosc.* **180**, 323–336 (1996).
8. A. G. Maki, W. Quapp, S. Klee, G. Mellau, and S. Albert, private communication.
9. Ralf Petry, Diplom thesis, Physikalisch-Chemisches Institut der Justus Liebig Universität Giessen, 1997.
10. J. W. C. Johns, *J. Mol. Spectrosc.* **125**, 442–464 (1987).
11. J. W. C. Johns and J. Van der Auwera, *J. Mol. Spectrosc.* **140**, 71–102 (1990).
12. C. DiLauro and I. M. Mills, *J. Mol. Spectrosc.* **21**, 386–413 (1966).
13. T. Nakagawa and Y. Morino, *Bull. Chem. Soc. Jpn.* **42**, 2212–2219 (1969).