was changed from *ABC* to *ACB*, 6.5 ma of 0.5-Mev deuterons were obtained. With helium ions, in the *ACB* mode, 1.5 ma of 1-Mev alpha particles was obtained. The measured energy gain per turn for He^{4++} and D_2^+ ions in this mode was approximately $5qV$.

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Hyperfine Structure in the *l*-Type Doubling Spectrum of HCN†

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Direct *l*-type transitions for HCN have been observed for $J=1$, 2, 3, 4, and 5. Values obtained of the asymmetry parameter $\eta=-0.082\pm0.005$ and the magnetic coupling constant $c_i=13\pm5$ kc/sec are in good agreement with previous work. For N^{14} the value $eq_mQ=-4.81\pm0.02$ Mc/sec is 5% higher than that obtained in the ground vibrational state. This change in eq_mQ can be explained by a decrease in the hybridization of the σ bond.

INTRODUCTION

DIRECT *l*-type doubling transitions of the linear molecule HCN have been observed by several investigators in the microwave *K* band.[1–3] For smaller values of J the spectrum lies in the *L* and *S* bands where some work has been reported.[4,5] The work reported herein is confined to the *L* and *S* bands.[6]

In the first excited bending mode the degenerate vibrational levels are split and it is the transition between these levels that gives rise to the *l*-type doubling spectrum. N^{14}, with its spin of one, produces a quadrupole splitting. This splitting normally results in a single $\Delta F=0$ line. White[3] has shown that this main line is further split due to an asymmetry of the electric field gradient at the nitrogen nucleus produced by the bending of the molecule.

At lower J values the relative intensities of the $\Delta F=\pm1$ lines increase and as a result these transitions for $J=3$ and 4 were observed. With this added information it was possible to evaluate the quadrupole coupling constant, the asymmetry parameter and the magnetic $\mathbf{I}\cdot\mathbf{J}$ interaction constant.

EXPERIMENTAL TECHNIQUE

A Stark-modulated spectrometer whose cell is a 20-foot *S*-band wave guide was used throughout. The guide operated in the usual TE_{01} mode for the $J=3$, 4, and 5 lines. Since the guide cutoff is 2000 Mc/sec, for the $J=1$ and 2 lines it was run as a transmission line in a *TEM* mode. A description of the apparatus is found elsewhere.[7]

EXPERIMENTAL RESULTS

Table I lists the lines observed, their frequencies and the parameters evaluated from this data. All the $\Delta F=\pm1$ transitions were observed for $J=3$. The $\Delta F=0$ splitting is theoretically threefold. The line found, however, was split twofold with the two higher frequency components unresolved. This is due to the fact that the lower of the two unresolved components has twice the intensity of the upper, plus the fact that the lines are separated by only 60 kc/sec. This observation is approximately true for all the reported lines save $J=1$. Since the $F=0\rightarrow F=0$ transition is forbidden, the $J=1$ $\Delta F=0$ splitting is theoretically twofold. The intensity ratio of these two lines is 5:1 and as a result only one line was observed for $J=1$. The $J=4$ line $\Delta F=\pm1$ transitions were seen only at the lower end of the spectrum because of interference from Stark components at the upper frequency end.

The second harmonic of a 707*A* klystron was employed as the signal source for the $J=4$ line. The result was gratifying in that not only was the $J=4$ line seen but the $J=5$ line as well. (See Fig. 1.) This came about as follows: The frequency of the *l*-type doubling transition is given as $\nu=qJ(J+1)$ where (see following section) q is approximately constant. Since the fundamental frequency used was $10q$, the frequency of the $J=4$ line $20q$, and the frequency of the $J=5$ line $30q$, the second and third harmonics of the signal source

† Supported by the U. S. Air Force, through the Office of Scientific Research of the Air Research and Development Command.
[1] R. G. Shulman and C. H. Townes, Phys. Rev. **77**, 421 (1950).
[2] T. L. Weatherly and D. Williams, Phys. Rev. **87**, 517 (1952).
[3] R. L. White, J. Chem. Phys. **23**, 249 (1955).
[4] R. J. Collier, Phys. Rev. **95**, 1201 (1954).
[5] Miyahara, Herakawa, and Shimoda, J. Phys. Soc. Japan **11**, 335 (1956).
[6] A preliminary account of this work by L. Yarmus appears in the Bull. Am. Phys. Soc. Ser. II, **1**, 13 (1956).
[7] Weisbaum, Beers, and Herrmann, J. Chem. Phys. **23**, 1601 (1955).

TABLE I. Measured frequencies and evaluated constants for l-type doubling spectrum of HCN.

J	Transition $F\rightarrow F'$	Measured frequency Mc/sec	Theoretical center frequency ν_0 × Mc/sec	Asymmetry parameter η	ηeq_mQ kc/sec	eq_mQ Mc/sec	I·J Magnetic interaction constant c_i kc/sec
1	2 2 }[a]	448.967±0.010	448.947±0.010				
	1 1 }						
2	2 2	1346.677±0.005	1346.758±0.006		323±15		
	3 3 }	1346.796±0.005					
	1 1 }						
3	3 3	2693.250±0.009	2693.349±0.010	−0.082±0.005	396±24	−4.81±0.020	13±5
	4 4 }	2693.395±0.006					
	2 2 }						
	2 3	2691.757±0.008					
	4 3	2692.071±0.006					
	3 4	2694.582±0.009					
	3 2	2694.954±0.009					
4	4 4	4488.381±0.020	4488.475±0.020	−0.079±0.016	377±75	−4.79±0.034	11±4
	5 5 }	4488.522±0.020					
	3 3 }						
	3 4	4486.762±0.013					
	5 4	4487.000±0.006					
5	5 5	6731.793±0.011	6731.881±0.007		352±34		
	6 6 }	6731.925±0.009					
	4 4 }						

[a] Bracket indicates that the two lines were not resolved. The frequency given is the measured composite of both.

gave rise to the $J=4$ and $J=5$ lines, respectively. The separation between these lines is direct experimental evidence of the variation of q with rotational quantum number J.

DISCUSSION OF RESULTS

The expression for the energy can be written as[8]

$$E=E_0+\frac{2J+3}{J}eq_mQ\left[\frac{3-J(J+1)}{(J+1)(2J+3)}\pm\frac{J}{2(2J+3)}\right]Y(F)+c_i\mathbf{I}\cdot\mathbf{J},$$

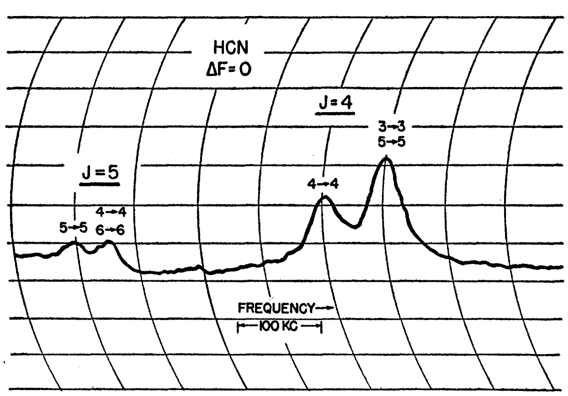

FIG. 1. Recorder trace of the $J=4$ and 5 $\Delta F=0$ transition in HCN.

where eq_mQ is the quadrupole coupling constant, η the asymmetry parameter, $Y(F)$ Casimir's function, and c_i the constant of the interaction between the spin of the nitrogen nucleus and the total rotation of the molecule J. By using this equation and the frequencies of the observed lines, the parameters are evaluated. For the $J=3$ and $J=4$ lines, all the parameters can be assigned values; for the $J=2$ and $J=5$ lines, only the theoretical center frequency and the product of eq_mQ and η can be found. The $J=1$ line yielded only the theoretical center frequency. Table I lists the results.

White,[3] from his $J=10$ line data, evaluated the product $eq_mQ\eta$ and his value of 392±8 kc/sec compares favorably with the results presented. Similarly the magnetic interaction constant $c_i=13\pm5$ kc/sec agrees with previous work.[9]

The value of eq_mQ in the present work (see Table I) is to be compared with the value −4.58±0.05 Mc/sec obtained by Simmons, Anderson, and Gordy[10] in the ground vibrational state. Thus it would appear that eq_mQ of HCN increases by some five percent in going from the ground vibrational state to the first excited bending mode. There are two possible theoretical approaches that can be considered to explain this difference; the molecular orbital "self-consistent" field calculations of Bassompierre[11] and the "valence shell" method of Townes and Dailey.[12] Bassompierre's calculation is probably the more accurate of the two but

[8] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

[9] R. L. White, Revs. Modern Phys. **27**, 276 (1955).

[10] Simmons, Anderson, and Gordy, Phys. Rev. **77**, 77 (1950).

[11] A. Bassompierre, Compt. rend. **239**, 1298 (1954); Compt. rend. **240**, 285 (1955); Discussions Faraday Soc. **19** (1955).

[12] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

because of its complexity it is difficult to obtain a simple physical explanation for the change in eq_mQ. Thus despite the fact that the Townes and Dailey method is probably less accurate, this is the approach that will be taken. It is interesting to note that Townes and Dailey[12] predict a value of $eq_mQ=-4.8$ Mc/sec for HCN in the ground vibrational state.

White,[3] following the arguments of Townes and Dailey, explains the $\Delta F=0$ splitting and the appearance of a negative η as the result of the preferential breaking of one of the π bonds when the ionic bond is formed. This hypothesis conforms with the values of η obtained in his as well as in this work, but does not predict any change in the quadrupole coupling constant. A possible means of accounting for the increase in eq_mQ is to postulate a decrease in the hybridization of the P_σ bond as a result of the molecular bending. When one replaces the assumed hybridized wave functions[12,3] (see especially Table I of reference 3)

$$\frac{1}{2}\psi_s+\frac{\sqrt{3}}{2}\psi_{p_z} \quad \text{and} \quad 2\times\left(\frac{\sqrt{3}}{2}\psi_s+\frac{1}{2}\psi_{p_z}\right)$$

by

$$a\psi_s+(1-a^2)^{\frac{1}{2}}\psi_{p_z} \quad \text{and} \quad 2\times[(1-a^2)^{\frac{1}{2}}\psi_s+a\psi_{p_z}],$$

the value of the parameter a is found by assuming the 5% increase in V_{zz}. The result is $a=0.51$. Thus the hybridized wave function takes the new form

$$0.51\psi_s+0.860\psi_{p_z}$$

in the first excited vibrational state $v_2=1$. The foregoing in no way conflicts with White's analysis to which recourse must be taken in accounting for the sign and magnitude of the asymmetry parameter.

Westerkamp[13] based on data from $J=6$ through $J=12$, empirically obtained a formula for the variation of q, the l-type doubling constant, with J. Subsequently, Miyahara, Herakawa, and Shimoda[5] based on some new measurements they made, constructed a new formula. Table II lists the measured frequencies ($J=1$ to 5 of this work, $J=6$ to 12 as reported by Westerkamp), the q evaluated from these measurements, as well as the q derived from both formulas. The agreement is somewhat better using the Miyahara formula. It is clear from both formulas that the $J=8$ line needs remeasuring.

[13] J. F. Westerkamp, Phys. Rev. 93, 716 (1954).

TABLE II. l-type doubling constant for HCN.[a]

J	ν_0 Measured frequency	$q=\frac{\nu_0}{J(J+1)}$	q_w from Westerkamp formula[b]	q_J from Miyahara formula[c]
1	448.947	224.473	224.466	224.473
2	1346.758	224.460	224.455	224.462
3	2693.349	224.446	224.440	224.446
4	4488.475	224.424	224.419	224.425
5	6731.881	224.396	224.393	224.398
6	9423.3	224.365	224.361	224.366
8	16 147.8	224.274	224.283	224.286
9	20 181.4	224.238	224.236	224.238
10	24 660.4	224.185	224.184	224.185
11	29 585.1	224.129	224.126	224.126
12	34 953.5	224.061	224.063	224.062

[a] All values shown are in Mc/sec.
[b] $q_w=224.471-0.002614J(J+1)$.
[c] $q_J=224.478-0.002667J(J+1)$.

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