Microwave and Millimeter Wave Spectra of Hydrazoic Acid*

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Five rotational transitions have been recorded for each of the abundant
species of hydrazoic acid and hydrazoic acid-d. Both molecules have normal
centrifugal distortion behavior. The spectroscopic constants derived from
the measurements are

$HN_3 - A_0 = 615,600 \pm 7000$ Mc/sec, $B_0 = 12,034.15 \pm 0.09$ Mc/sec,
$\quad C_0 = 11,781.51 \pm 0.09$ Mc/sec, $D_{JK} = 787.8 \pm 5.4$ kc/sec,
$\quad D_J = 5.09 \pm 0.54$ kc/sec, $H_{JKK} = -1.13 \pm 0.15$ kc/sec,
$\quad H_{JJK} = 0.03 \pm 0.03$ kc/sec.

$DN_3 - A_0 = 351,500 \pm 7000$ Mc/sec, $B_0 = 11,350.23 \pm 0.05$ Mc/sec,
$\quad C_0 = 10,965.48 \pm 0.05$ Mc/sec, $D_{JK} = 442.6 \pm 2.4$ kc/sec,
$\quad D_J = 4.22 \pm 0.17$ kc/sec, $H_{JKK} = -0.21 \pm 0.08$ kc/sec,
$\quad H_{JJK} = -0.03 \pm 0.02$ kc/sec.

An important part of the study was a reinvestigation of the $J = 0 \rightarrow 1$ transi-
tion of HN_3 which gave $eq_{aa}Q = +4.65 \pm 0.25$ Mc/sec for the NH nitrogen N^{14}
nucleus.

I. INTRODUCTION

In a recent paper (*1*) we described the mysterious centrifugal distortion effects
which were found in the millimeter wave spectra of isocyanic acid, HNCO, and
isothiocyanic acid, HNCS. The only other stable pseudohalogen acid which
has a close structural resemblance to these two molecules is hydrazoic acid,
HN_3 (see Fig. 1), which makes it a logical selection for study if further informa-
tion on centrifugal stretching behavior in this type of slightly asymmetric rotor
is to be obtained. The main idea behind the present work was therefore to see
how the somewhat more asymmetric molecules HN_3 and DN_3 would compare
with HNCO, DNCO, HNCS, and DNCS as regards centrifugal distortion.

II. EXPERIMENTAL

For almost all of the observations the apparatus used was the same as that in
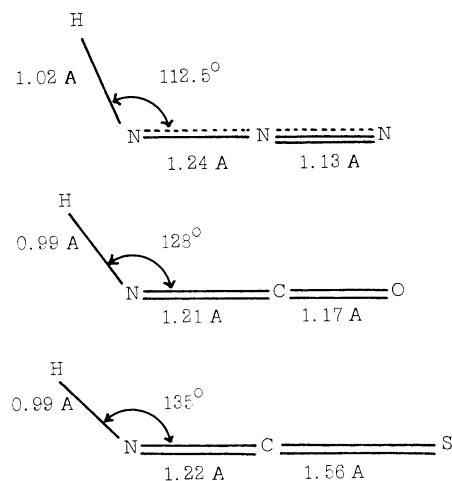the HNCO-HNCS investigation and as described previously (*2*). Frequency

Fig. 1. Molecular structural parameters of hydrazoic, isocyanic, and isothiocyanic acids.

measurements in the millimeter wave region were made between 60,000 and 180,000 Mc sec (0.17–0.50 mm). The frequencies were checked against the WWV 5 Mc sec standard signal and are considered to be accurate to about 0.25 Mc sec. During the measurements the gas in the absorption cell was maintained at a pressure of about 10^{-2} mm of mercury and at a temperature of $-78°C$. When making accurate measurements of the quadrupole hyperfine splitting in the rotational spectrum of HN_3 a standard Stark modulation spectrometer was employed, operating close to 23,815 Mc sec. A 0–500 volt square wave generator working at 91 kc sec provided the modulation.

Hydrazoic acid was most commonly prepared by the action of phosphoric acid, made by dissolving phosphorus pentoxide in water, on sodium azide, NaN_3. However, sulfuric, acetic, and stearic acids were also used with satisfactory results. Hydrazoic acid-d was made by reacting the sodium azide with deutero-phosphoric acid, produced by refluxing a P_2O_5–D_2O mixture for three days at 90°. This gave a much better yield of DN_3 than that obtained by using deutero-stearic acid, prepared by exchanging $C_{17}H_{35}COOH$ with D_2O, because of the low solubility of this acid in water.

III. FREQUENCIES AND ROTATIONAL CONSTANTS

Five a-type, R-branch, rotational transitions were recorded for the ground vibrational state of each of the species HN_3^{14} and DN_3^{14}. They were:

$$HN_3^{14}: J = 0 \rightarrow 1, 3 \rightarrow 4, 4 \rightarrow 5, 5 \rightarrow 6, \text{ and } 6 \rightarrow 7$$
$$DN_3^{14}: J = 2 \rightarrow 3, 3 \rightarrow 4, 4 \rightarrow 5, 5 \rightarrow 6, \text{ and } 7 \rightarrow 8.$$

The calculated and observed frequencies for these transitions are listed in Table I and II. The values of total angular momentum quantum number, F,

are given only when the quadrupole hyperfine splitting could be resolved. Where F is not given the splitting was too small for the separate components to be seen and, in such a case of high J and low K, the observed frequency was assumed to correspond to the strongest line in the pattern. Negligible error is produced by this assumption.

TABLE I. HN$_3$ Line Frequencies

Transition		K	Observed Frequency (Mc/sec)	Calculated Frequency (Mc/sec)
$J = 0 \rightarrow 1$				
$0_{00} - 1_{01}$ $F = 1 - 0$		0	23,813.55	23,813.34
$F = 1 - 2$		0	23,815.58	23,815.37
$F = 1 - 1$		0	23,817.04	23,816.83
$J = 3 \rightarrow 4$				
$3_{03} - 4_{04}$		0	95,260.50	95,260.57
$3_{12} - 4_{13}$		1	95,760.15	95,760.24
$3_{13} - 4_{14}$		1	94,749.42	94,749.51
$3_{21} - 4_{22}$	$F = 3 - 4$	2	95,237.03	95,237.24
	$F = 4 - 5$ $F = 2 - 3$	2	95,236.17	95,236.38
$3_{22} - 4_{23}$	$F = 3 - 4$			
	$F = 4 - 5$ $F = 2 - 3$	2	95,235.45	95,235.66
$3_{30} - 4_{41}$ $F = 3 - 4$		3	95,205.12	95,205.28
$3_{31} - 4_{32}$ $F = 4 - 5$ $F = 2 - 3$		3	95,203.10	95,203.26

TABLE I. HN_3 Line Frequencies (continued)

Transition	K	Observed Frequency (Mc/sec)	Calculated Frequency (Mc/sec)
$J = 4 \rightarrow 5$			
$4_{04} - 5_{05}$	0	119,074.12	119,074.17
$4_{13} - 5_{14}$	1	119,698.95	119,699.09
$4_{14} - 5_{15}$	1	118,435.82	118,435.96
$4_{22} - 5_{23}$	2	119,044.95	119,045.48
$4_{23} - 5_{24}$	2	119,043.41	119,043.94
$4_{31} - 5_{32}$ $\quad F = 4 - 5$	3	119,004.33	119,004.82
$4_{32} - 5_{33}$ $\quad F = 5 - 6$ $\quad F = 3 - 4$	3	119,003.46	119,003.95
$4_{40} - 5_{41}$ $4_{41} - 5_{42}$	4	118,946.42[a]	118,946.35
$J = 5 \rightarrow 6$			
$5_{05} - 6_{06}$	0	142,886.92	142,886.78
$5_{14} - 6_{15}$	1	143,637.49	143,637.28
$5_{15} - 6_{16}$	1	142,121.48	142,122.70
$5_{23} - 6_{24}$	2	142,853.84	142,854.16
$5_{24} - 6_{25}$	2	142,851.03	142,851.10
$5_{32} - 6_{33}$ $5_{33} - 6_{34}$	3	142,803.67	142,803.88

TABLE I. HN$_3$ Line Frequencies (continued)

Transition	K	Observed Frequency (Mc/sec)	Calculated Frequency (Mc/sec)
J = 5 → 6 (continued)			
$5_{41} - 6_{42}$ F = 5 — 6	4	142,735.63	142,735.61
F = 6 — 7 $5_{42} - 6_{43}$ F = 4 — 5	4	142,734.66	142,734.64
$5_{50} - 6_{51}$ $5_{51} - 6_{52}$	5	142,644.26[a]	142,644.36
J = 6 → 7[b]			
$6_{06} - 7_{07}$	0	166,698.40	166,698.20
$6_{15} - 7_{16}$	1	167,575.07	167,574.96
$6_{16} - 7_{17}$	1	165,806.33	165,806.22
$6_{24} - 7_{25}$	2	166,662.05	166,662.20
$6_{25} - 7_{26}$	2	166,657.66	166,657.76
$6_{33} - 7_{34}$ $6_{34} - 7_{35}$	3	166,602.85	166,602.91
$6_{42} - 7_{43}$ $6_{43} - 7_{44}$	4	166,522.79	166,522.54
$6_{51} - 7_{52}$ $6_{52} - 7_{53}$	5	166,416.76	166,416.86

[a] Line too weak for hyperfine structure to be resolved.

[b] K = 6 component is too weak to be observed.

TABLE II. DN_3 Line Frequencies

Transition		K	Observed Frequency (Mc/sec)	Calculated Frequency (Mc/sec)
$J = 2 \rightarrow 3$				
$2_{02} - 3_{03}$		0	66,945.50	66,945.40
$2_{11} - 3_{12}$		1	67,520.75	67,520.82
$2_{12} - 3_{13}$		1	66,366.68	66,366.75
$2_{20} - 3_{21}$	$F = 2 - 3$	2	66,938.71	66,938.54
$2_{20} - 3_{21}$ $\quad F = 3 - 4$ $2_{21} - 3_{22}$ $\quad F = 2 - 3$		2	66,937.27	66,937.10
$2_{20} - 3_{21}$ $\quad F = 1 - 2$ $2_{21} - 3_{22}$ $\quad F = 3 - 4$		2^a	66,935.94	66,935.77
$J = 3 \rightarrow 4$				
$3_{03} - 4_{04}$		0	89,258.55	89,258.51
$3_{12} - 4_{13}$		1	90,026.99	90,027.05
$3_{13} - 4_{14}$		1	88,488.03	88,488.09
$3_{21} - 4_{22}$	$F = 3 - 4$	2	89,251.21	89,251.10
	$F = 4 - 5$ $F = 2 - 3$	2	89,250.42	89,250.31
$3_{22} - 4_{23}$	$F = 3 - 4$	2	89,247.84	89,247.73
	$F = 4 - 5$ $F = 2 - 3$	2	89,247.11	89,247.00

TABLE II. DN$_3$ Line Frequencies (continued)

Transition		K	Observed Frequency (Mc/sec)	Calculated Frequency (Mc/sec)
J = 3 → 4 (continued)				
$3_{30} - 4_{31}$ F = 3 — 4		3	89,231.45	89,231.59
F = 4 — 5				
$3_{31} - 4_{32}$ F = 2 — 3		3	89,229.74	89,229.88
J = 4 → 5				
$4_{04} - 5_{05}$		0	111,569.92	111,569.93
$4_{13} - 5_{14}$		1	112,532.50	112,532.44
$4_{14} - 5_{15}$		1	110,608.76	110,608.70
$4_{22} - 5_{23}$ F = 4 — 5		2	111,564.81	111,564.72
F = 5 — 6		2	111,564.52	111,564.43
F = 3 — 4				
$4_{23} - 5_{24}$ F = 4 — 5		2	111,558.09	111,558.00
F = 5 — 6		2	111,557.82	111,557.73
F = 3 — 4				
$4_{31} - 5_{32}$ F = 4 — 5		3	111,537.86	111,537.98
F = 5 — 6		3	111,536.98	111,537.10
$4_{32} - 5_{33}$ F = 3 — 4				
$4_{40} - 5_{41}$ F = 4 — 5		4	111,506.13	111,506.52
F = 5 — 6		4	111,504.67	111,505.06
$4_{41} - 5_{42}$ F = 3 — 4				

TABLE II. DN_3 Line Frequencies (continued)

Transition	K	Observed Frequency (Mc/sec)	Calculated Frequency (Mc/sec)
$J = 5 \rightarrow 6$			
$5_{05} - 6_{06}$	0	133,879.14	133,879.21
$5_{14} - 6_{15}$	1	135,036.98	135,036.82
$5_{15} - 6_{16}$	1	132,728.67	132,728.51
$5_{23} - 6_{24}$	2	133,879.14	133,879.13
$5_{24} - 6_{25}$	2	133,867.80	133,867.79
$\left.\begin{array}{l} 5_{32} - 6_{33} \\ 5_{33} - 6_{34} \end{array}\right\}$	3	133,844.21	133,844.15
$\left.\begin{array}{l} 5_{41} - 6_{42} \\ 5_{42} - 6_{43} \end{array}\right\}$	4	133,805.16	133,805.64
$\left.\begin{array}{l} 5_{50} - 6_{51} \\ 5_{51} - 6_{52} \end{array}\right\}$	5	133,756.98	133,756.36
$J = 7 \rightarrow 8^{b}$			
$7_{07} - 8_{08}$	0	178,489.31	178,489.64
$7_{16} - 8_{17}$	1	180,042.27	180,042.41
$7_{17} - 8_{18}$	1	176,964.18	176,964.32
$7_{25} - 8_{26}$	2	178,512.13	178,511.81
$7_{26} - 8_{27}$	2	178,484.73	178,484.41

TABLE II. DN_3 Line Frequencies (continued)

Transition	K	Observed Frequency (Mc/sec)	Calculated Frequency (Mc/sec)
$J = 7 \rightarrow 8^{b}$ (continued)			
$7_{34} - 8_{35}$ $7_{35} - 8_{36}$	3	178,456.64	178,456.34
$7_{43} - 8_{44}$ $7_{44} - 8_{45}$	4	178,404.21	178,404.09
$7_{52} - 8_{53}$ $7_{53} - 8_{54}$	5	178,337.49	178,337.79

[a] The component $2_{21} \rightarrow 3_{22}$, $F = 1 \rightarrow 2$ was too weak to be observed.

[b] The components K = 6 and 7 were too weak to be observed.

To obtain the calculated frequencies of Tables I and II the following procedure was adopted:

(a). A correction for the very slight degree of asymmetry was applied to the observed frequencies. The magnitude of this correction for a particular line was calculated from the observed splitting of the components with $K_{-1} = 2$ in the observed transition with the highest J for the molecule, i.e., for HN_3 the splitting of the lines $6_{24} \rightarrow 7_{25}$ and $6_{25} \rightarrow 7_{26}$ and for DN_3 the splitting of $7_{25} \rightarrow 8_{26}$ and $7_{26} \rightarrow 8_{27}$. Such a pair of $K = 2$ components are equally affected by quadrupole splitting.

(b). A correction for the nuclear quadrupole effects was made to each of the frequencies obtained from (a) above using the value $+4.65$ Mc sec for the main N^{14} coupling constant (see Section IV below).

(c). The frequencies from (b) were subjected to a least squares fit to the

formula

$$\nu = (B_0 + C_0)(J + 1) - 2 D_{JK} K^2(J + 1) - 4 D_J (J + 1)^3$$
$$+ 2 H_{JJK} K^2 (J + 1)^3 + 4 H_{JKK} K^4(J + 1) \tag{1}$$
$$+ H_{JJJ} (J + 1)^3 [(J + 2)^3 - J^3]$$

using an IBM 7072 computor. Here $(B_0 + C_0)$ has replaced $2 B_0$ in the exactly symmetric top expression. The effect of the H_{JJJ} term was found to be negligibly small so it was neglected in order to simplify the computer program. This program gave calculated frequencies which were corrected back to give the calculated frequencies of Tables I and II. The same program gave also values for $(B_0 + C_0)$, D_J, D_{JK}, H_{JJK}, and H_{JKK}. The magnitude of the quantity $(B_0 - C_0)$ was found from the separations of the $K = 1$ components, $(B_0 - C_0)(J + 1)$. The rotational and centrifugal distortion constants for HN_3 and DN_3 are shown in Table III. A separate program was used to invert the 5×5 normal equations matrix of the least squares analysis so as to obtain the errors in the derived constants.

No absorption peaks which could be attributed to rotational transitions of vibrational excited molecules were observed even when the absorption cell was allowed to warm to room temperature.

IV. NUCLEAR QUADRUPOLE EFFECTS

In an earlier investigation of the $J = 0 \rightarrow 1$ transition of HN_3 (3) it was reported that the observed quadrupole pattern could be accounted for in terms of a single N^{14} nucleus with $eqQ = -4.67$ Mc sec. For the transitions observed in the millimeter wave region, which involve higher J values, the hyperfine splitting is only sufficient to separate the strong component $F = J \rightarrow J + 1$ from the other two intense components $F = J + 1 \rightarrow J + 2$ and $F = J - 1 \rightarrow J$ which could not be resolved and thus appear as a single line. Such a separation into two observed lines occurs only for the higher K-components. In the present millimeter wave observations the splitting between the $F = J \rightarrow J + 1$ component and the combined components $F = J + 1 \rightarrow J + 2$ and $F = J - 1 \rightarrow J$ was always too small to measure with any accuracy and the uncertainty in the exact position of $F = J + 1 \rightarrow J + 2$ and $F = J - 1 \rightarrow J$ lines makes it difficult to get a good eqQ value from the measurements. However the relative intensities of the two lines observed in such a case are directly related to the sign of this main quadrupole coupling constant, and in all cases where partial resolution was possible the intensities were such as to indicate the sign to be positive. To confirm this suggestion a Stark modulation spectrometer was used to reinvestigate the $J = 0 \rightarrow 1$ of HN_3. Splitting into three hyperfine components, two of which showed broadening due to a second nitrogen nucleus, was easily achieved (see Fig. 2). Measurement of the tops of the peaks gave a value of $+4.65$ Mc sec for the largest N^{14} quadrupole coupling constant.

TABLE III. Spectroscopic Constants of HN_3 and DN_3

Constants		HN_3		DN_3	
$B_o + C_o$	(Mc/sec)	23,815.66	$\pm$ 0.08	22,315.71	$\pm$ 0.03
$B_o - C_o$	(Mc/sec)	252.65	$\pm$ 0.05	384.74	$\pm$ 0.03
B_o	(Mc/sec)	12,034.15	$\pm$ 0.09	11,350.23	$\pm$ 0.05
I_b^o	(amu A^2)	42.00803	$\pm$ 0.00029	44.53929	$\pm$ 0.00017
C_o	(Mc/sec)	11,781.51	$\pm$ 0.09	10,965.48	$\pm$ 0.05
I_c^o	(amu A^2)	42.90886	$\pm$ 0.00030	46.10202	$\pm$ 0.00018
A_o	(Mc/sec)	615,600	$\pm$ 7000	351,500	$\pm$ 7000
I_a^o	(amu A^2)	0.8212	$\pm$ 0.0092	1.4382	$\pm$ 0.0281
δ	(amu A^2)	0.0796		0.1245	
$(I_c^o - I_b^o - I_a^o)$					
D_{JK}	(kc/sec)	787.8	$\pm$ 5.4	442.6	$\pm$ 2.4
D_J	(kc/sec)	5.09	$\pm$ 0.54	4.22	$\pm$ 0.17
H_{JKK}	(kc/sec)	-1.13	$\pm$ 0.15	-0.21	$\pm$ 0.08
H_{JJK}	(kc/sec)	0.03	$\pm$ 0.03	-0.03	$\pm$ 0.02
b_p		-20.9×10^{-5}		-56.0×10^{-5}	
$\varkappa$		-0.99916		-0.99774	
$eq_{aa}Q$ (NH nitrogen)	(Mc/sec)	+4.65	$\pm$ 0.25	—	

The positive sign for the main coupling constant shows that in HN_3 the N^{14} nucleus responsible for the largest splitting has an entirely different electronic environment from the N^{14} in HCN, CH_3CN, BrCN or NH_3 where eqQ (N^{14}) is near to -4 Mc sec in each molecule (4). The value of eqQ for the terminal nitrogen of N_2O, a molecule with a similar heavy atom arrangement to HN_3 and also isoelectronic with it, is -1.03 Mc sec (5) and the central nitrogen in the same molecule has $eqQ = -0.27$ Mc sec (6). It is evident therefore that the eqQ of
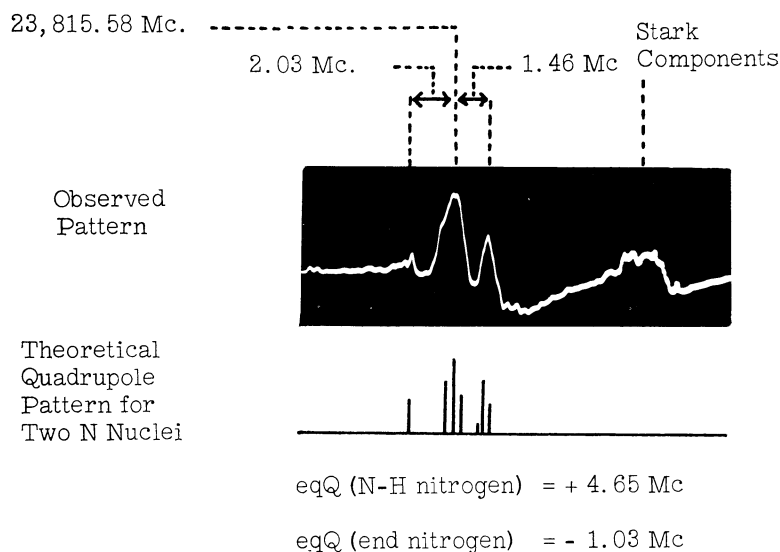
23,815.58 Mc. - - - - - - - - - - - - - - -
                                                    Stark
    2.03 Mc. - - - -   - - - - 1.46 Mc   Components

Observed
Pattern

Theoretical
Quadrupole
Pattern for
Two N Nuclei

eqQ (N-H nitrogen) = + 4.65 Mc

eqQ (end nitrogen)   = - 1.03 Mc

Fig. 2. The $J = 0 \rightarrow 1$ transition of HN_3, showing the main quadrupole splitting, due to the NH nitrogen N^{14} nucleus.

+4.65 Mc sec. in HN_3 can only be that of the NH nitrogen nucleus. The value can be compared to $eqQ = +1.2$ and $+2.00$ Mc sec for the N^{14} nucleus in HNCS and HNCO respectively (7). When obtaining the calculated pattern of Fig. 2 it was assumed that the terminal nitrogens in N_2O and HN_3 have the same electronic environment. Our conclusion concerning the assignment of the +4.65 Mc/sec coupling constant in HN_3 has recently been confirmed by a high resolution study conducted by Forman and Lide (8) on the same transition of HN_3, $J = 0 \rightarrow 1$. By using N^{15} substituted species they were able to observe independently the quadrupole effects of the NH and end nitrogens and obtained the $eq_{aa}Q$ values +4.85 and −1.35 Mc sec, respectively, for these two nuclei.

The most important contributing electron structures for HN_3 are

$$\overset{-}{HN} - \overset{+}{N} \equiv N \quad \text{and} \quad HN = \overset{+}{N} = \overset{-}{N}.$$
$$\text{(A)} \qquad\qquad\qquad \text{(B)}$$

Taking the NH nitrogen to have tetrahedral hybridization in (A) and trigonal hybridization in (B), putting the screening factor $(1 + c) = 1.25$ (4), and assuming 15% ionic character for the NH bond (9) in both (A) and (B) then the number of unbalanced p-electrons for each structure is estimated to be

$$U_p (A) = + 0.41 \quad \text{and} \quad U_p (B) = + 0.09.$$

The N—H bond lengths (Fig. 1) indicate approximately 44% weight for Struc-

ture (A) neglecting, however, any effect which the separated charges may have on the internuclear distances. The over-all U_p is thus estimated to be

$$U_{p(\text{total})} = +0.23.$$

Comparison of this figure with the observed quantity $+4.85$ Mc/sec for the coupling constant of the NH nitrogen gives the value -21 Mc/sec for the coupling constant per unbalanced p-electron, $eq_{210} Q$, for the N^{14} nucleus.

This value does not compare well with that obtained by using a similar procedure on the ammonia molecule. If the same values of $(1 + \epsilon)$ and ionic character are used as above and 18% s-character is attributed to the bonding orbitals then for NH_3 it is estimated that

$$U_{p(\text{total})} = -0.43.$$

The observed eqQ (N^{14}) for ammonia is -4.084 Mc/sec (10) which, together with the value -0.43 for U_p gives $eq_{210} Q(N^{14})$ as -9.5 Mc/sec. Correspondence between this value and the one found from the above calculations on HN_3 is clearly unsatisfactory. The different signs of U_p for NH_3 and for the NH nitrogen of HN_3 do, however, agree with the experimental facts.

If simple considerations are applied to the end nitrogen of HN_3, yet another value of $eq_{210} Q(N^{14})$ results. Assuming that the electrons which contribute significantly to U_p are in two $p\pi$ orbitals and sp bonding and sp antibonding orbitals with 50% s-character, for both Structure (A) and Structure (B) then we find that for the end nitrogen:

$$U_{p(\text{total})} = -0.22.$$

The observed $eq_{aa} Q$ for this nitrogen (8) is -1.35 so these two figures correspond to a value of -6.1 Mc/sec for $eq_{210} Q(N^{14})$. It is clear therefore that although these simple treatments give consistent results as regards the sign of $eq_{210} Q(N^{14})$, something more is needed to produce quantitative agreement.

V. CENTRIFUGAL DISTORTION

The millimeter wave spectra of the six molecules HNCS, DNCS, HNCO, DNCO, HN_3 and DN_3 have now been investigated and appear to fall into two classes (Fig. 3.)

HNCO, HN_3, and DN_3 all behave normally with respect to centrifugal stretching in that asymmetry and quadrupole corrected frequencies for each molecule obey the relationship of Eq. (1). In each of these three cases D_{JK} is positive.

DNCO, HNCS, and DNCS are abnormal. Equation (1) is not a satisfactory expression for the frequencies in the rotational spectra of these three molecules and also D_{JK} appears to have a negative sign.

It is strange that the most symmetric molecule of the six, HNCS, (see Table IV) fits worst to the symmetric top relation Eq. (1) while the most asymmetric

molecule, DN_3, fits best. It is also interesting that the K-pattern reversal takes place between HNCO and DNCO but not between HNCS and DNCS or HN_3 and DN_3. Again there appears to be no special relation between the precise amount of asymmetry and the centrifugal stretching behavior exhibited. DNCO
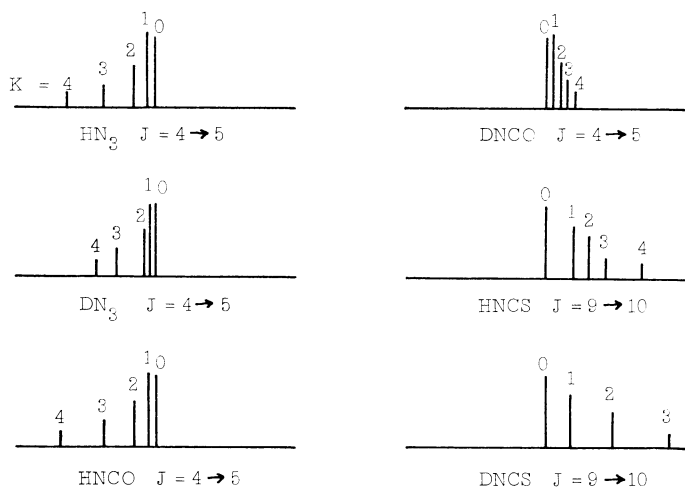

FIG. 3. Centrifugal distortion effects in the millimeter wave spectra of hydrazoic, isocyanic, isothiocyanic acids and their deuterated forms. The observed frequencies have been corrected for the small quadrupole and asymmetry effects.

TABLE IV. Asymmetry Parameters for Isocyanic, Isothiocyanic and Hydrazoic Acids.

Molecule	$b_p \times 10^5$	$\varkappa$
HNCS	-1.28	-0.99995
DNCS	-3.85	-0.99985
HNCO	-3.49	-0.99966
DNCO	-22.3	-0.99911
HN_3	-20.9	-0.99916
DN_3	-56.0	-0.99774

and HN$_3$ have about the same asymmetry but opposite patterns. The only quali-tative conclusion is that the behavior over the series of six molecules seems to be opposite of the usual increase in symmetric top characteristics with decreasing asymmetry. The very large a-axis components of angular momentum are the most likely cause of these apparent anomalies (1).

VI. ACKNOWLEDGMENTS

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