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The Millimeter Wave Spectra of Isocyanic and  
Isothiocyanic Acids

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## The Millimeter Wave Spectra of Isocyanic and Isothiocyanic Acids\*

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An investigation of the mm-wave rotational spectra of the very slightly asymmetric tops HNCS, DNCS, HNC<sub>0</sub> and DNC<sub>0</sub> has been carried out in the frequency range 80 000-190 000 Mc/sec. Several *R*-branch, *a*-type, transitions were observed for each molecule and the rotational constants  $A_0$ ,  $B_0$ , and  $C_0$  were determined for the four species containing the most abundant isotopes of N, C, O, or S.  $B_0$  and  $C_0$  were also found for HNCS<sup>34</sup>. The centrifugal distortion constant  $D_J$  was obtained for each abundant form. The constants are HNCS:

$$\begin{aligned} A_0 &= 1\,483\,000 \pm 167\,000 \text{ Mc/sec}, B_0 = 5883.42 \pm 0.02 \text{ Mc/sec}, \\ C_0 &= 5845.62 \pm 0.02 \text{ Mc/sec}, D_J = 1.17 \pm 0.05 \text{ Kc/sec}; \text{DNCS:} \\ A_0 &= 723\,400 \pm 25\,000 \text{ Mc/sec}, B_0 = 5500.51 \pm 0.05 \text{ Mc/sec}, \\ C_0 &= 5445.26 \pm 0.05 \text{ Mc/sec}, D_J = 1.22 \pm 0.31 \text{ Kc/sec}; \text{HNC}_0^{34}: \\ B_0 &= 5744.81 \pm 0.20 \text{ Mc/sec}, C_0 = 5708.73 \pm 0.20 \text{ Mc/sec}; \text{HNC}_0: \\ A_0 &= 956\,400 \pm 50\,000 \text{ Mc/sec}, B_0 = 11\,071.02 \pm 0.05 \text{ Mc/sec}, \\ C_0 &= 10\,910.58 \pm 0.05 \text{ Mc/sec}, D_J = 3.5 \pm 0.5 \text{ Kc/sec}; \text{DNC}_0: \\ A_0 &= 534\,500 \pm 70\,000 \text{ Mc/sec}, B_0 = 10\,313.61 \pm 0.05 \text{ Mc/sec}, \\ C_0 &= 10\,079.67 \pm 0.05 \text{ Mc/sec}, D_J = 2.9 \pm 0.5 \text{ Kc/sec}. \end{aligned}$$

The centrifugal distortion *K*-pattern is different in character for each of the four molecules. Agreement between calculation and experiment is obtained for HNC<sub>0</sub> and DNC<sub>0</sub> with the additional constants; HNC<sub>0</sub>:  $D_{JK} = +837$  Kc/sec,  $H_{JJK} = -0.056$  Kc/sec,  $H_{JKK} = +2.81$  Kc/sec. DNC<sub>0</sub>:  $D_{JK} = -227.1$  Kc/sec,  $H_{JJK} = +0.15$  Kc/sec,  $H_{JKK} = -5.61$  Kc/sec,  $H_{JJJ} = 0$ , utilizing the expression given by Costain. This expression gives a poor fit for DNCS and no fit for HNCS, and at present no treatment has been found to fit or explain satisfactorily the *K*-patterns for these two molecules.

An improved molecular structure has been calculated for HNCS the structural parameters being revised to  $r(\text{H}-\text{N}) = 0.988_7 \pm 0.003$  A,  $r(\text{N}-\text{C}) = 1.216_4 \pm 0.007$  A,  $r(\text{C}-\text{S}) = 1.560_5 \pm 0.003$  A  $\angle \text{H}-\text{N}-\text{C} = 134^\circ 59' \pm 10'$ .

A number of lines due to rotational transitions of vibrationally excited molecules were also observed and are assigned to the states  $v_5 = 1$  and  $v_6 = 1$  for HNCS and HNC<sub>0</sub> and probably, in addition,  $v_4 = 1$  for DNCS.

### I. INTRODUCTION

The microwave spectra of isocyanic acid, HNC<sub>0</sub>, and isothiocyanic acid, HNCS, have been previously recorded (1-3). Each molecule is a slightly asym-

\* The study was supported by the Air Force Office of Scientific Research.

metric rotor having a linear chain of three heavy atoms with the hydrogen atom off the heavy-atom axis and attached directly to nitrogen. All the earlier measurements were made near the  $K$ -band region in the frequency range 20 300–23 600 Mc/sec. Although a number of isotopic modifications were studied for each molecule only one transition was observed in each case,  $J = 2 \leftarrow 1$  for HNCS and  $J = 1 \leftarrow 0$  for HNCO. The rotational constants obtained from those spectra are slightly inaccurate because the magnitudes of the centrifugal stretching terms were unknown. A limitation for HNCO was that the rotational constants  $B_0$  and  $C_0$  could not be separately determined, only the sum ( $B_0 + C_0$ ) for the different isotopic species.  $A_0$  cannot be found for HNCS or HNCO or any of their isotopically substituted forms from these low frequency  $K$ -band rotational spectra.

An investigation of the mm-wave spectra of the two acids was therefore carried out to obtain more accurate values of  $B_0$  and  $C_0$ , to measure  $A_0$  for the most abundant isotopic forms of HNCS, DNCS, HNCO, and DNCO, and also to study centrifugal distortion effects in these molecules. The latter requires the observation of absorption lines for which the quantum number  $K_{-1}$  has higher values than  $K_{-1} = 1$ , which, since  $K_{-1} \leq J$ , was not possible in the earlier cm region work.

## II. EXPERIMENTAL

The sample of HNCO was prepared by heating pure, dry, cyanuric acid,  $(\text{HNCO})_3$ , to 600°C in a stream of dry argon. The monomeric HNCO was collected at  $-180^\circ\text{C}$ , distilled from  $-78^\circ\text{C}$  to  $-180^\circ\text{C}$  and then stored at  $-78^\circ\text{C}$  under vacuum. The vapor pressure of HNCO at this temperature is about 1–2 mm of mercury so that charges of vapor could be directly admitted to the absorption cell from the storage vessel. In observing the spectrum pressures of  $10^{-2}$ – $10^{-3}$  mm of mercury were used in the cell which was maintained at  $-78^\circ\text{C}$  for observing lines from molecules in the ground vibrational state and at room temperature when studying the much weaker vibrational satellites. DNCO was prepared as above by first allowing cyanuric acid to exchange with deuterium oxide for three to four days at about  $90^\circ\text{C}$ .

HNCS was prepared by mixing together dry, powdered, samples of potassium thiocyanate and potassium hydrogen sulfate and heating the mixture under vacuum. The pressures used during observation were similar to those for HNCO but the cell temperature was not taken below  $0^\circ\text{C}$  because the considerably lower vapor pressure of HNCS does not allow the observation of spectral lines for temperatures less than about  $-10^\circ\text{C}$ . DNCS was made by first exchanging potassium hydrogen sulfate with deuterium oxide and then using the  $\text{KDSO}_4$  in the same procedure as above.

The mm-wave spectrometer is essentially the same as that described by Venkateswarlu, Baker, and Gordy (4). The frequency measurements were based on the WWV standard 5 Mc/sec signal and are considered to be accurate to

between 0.25 and 0.5 Mc/sec for strong lines and to about 1 Mc/sec for the weaker lines coming from molecules in excited vibrational states. When studying the  $\text{HNCS}^{34}$  spectrum, a sample of  $\text{HNCS}$  containing  $\text{S}^{34}$  in its natural isotopic concentration was used. For  $\text{HNC}^{13}\text{S}$  the lines were not sufficiently intense to be measured by video detection.

### III. OBSERVED TRANSITION FREQUENCIES FOR MOLECULES IN THE GROUND VIBRATIONAL STATE

Several transitions were observed for each of the species  $\text{HNCO}$ ,  $\text{DNCO}$ ,  $\text{HNCS}$ , and  $\text{DNCS}$  (with N, C, and O or S the most common isotopes in each case) and one transition for  $\text{HNCS}^{34}$  was also recorded. Frequency measure-

TABLE I  
FREQUENCIES OF  $\text{HNCO}$  LINES FROM MOLECULES IN THE  
GROUND VIBRATIONAL STATE

Transition	K	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)
<u>J = 4 ← 3</u>			
$4_{04} - 3_{03}$	0	87,925.45	87,925.30
$4_{14} - 3_{13}$	1	87,597.03	87,597.89
$4_{13} - 3_{12}$	1	88,239.03	88,239.65
$4_{23} - 3_{22}$	2	87,898.53	87,898.99
$4_{22} - 3_{21}$	2		87,899.20
$4_{32} - 3_{31}$	3	87,867.60	87,867.42
$4_{31} - 3_{30}$	3	87,866.82	87,866.59
			87,866.53
<u>J = 5 ← 4</u>			
$5_{05} - 4_{04}$	0	109,905.90	109,905.82
$5_{15} - 4_{14}$	1	109,495.71	109,496.67
$5_{14} - 4_{13}$	1	110,297.82	110,298.87
$5_{24} - 4_{23}$	2	109,872.60	109,873.02
$5_{23} - 4_{22}$	2	109,872.99	109,873.43
$5_{33} - 4_{32}$	3	109,833.84	109,833.20
$5_{32} - 4_{31}$	3	109,833.45	109,832.81
			109,832.89

TABLE I (continued)  
 FREQUENCIES OF HNCO LINES FROM MOLECULES IN THE  
 GROUND VIBRATIONAL STATE

Transition	K	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)
<u>J = 5 ← 4 (continued)</u>			
$5_{42} - 4_{41}$	4	109, 778. 94	109, 779. 46
$5_{41} - 4_{40}$	4	109, 778. 37	109, 778. 76
			109, 778. 92
<u>J = 6 ← 5</u>			
$6_{06} - 5_{05}$	0	131, 885. 52	131, 885. 82
$6_{16} - 5_{15}$	1	131, 394. 40	131, 394. 99
$6_{15} - 5_{14}$	1	132, 356. 76	132, 357. 64
$6_{25} - 5_{24}$	2	131, 845. 56 <sup>a</sup>	131, 846. 62
$6_{24} - 5_{23}$	2	131, 846. 28 <sup>a</sup>	131, 847. 33
$6_{34} - 5_{33}$	3	131, 799. 12	131, 798. 55
$6_{33} - 5_{32}$	3		131, 798. 55
$6_{43} - 5_{42}$	4	131, 734. 00	131, 733. 78
$6_{42} - 5_{41}$	4	131, 733. 64	131, 733. 61
			131, 733. 67
$6_{52} - 5_{51}$	5	131, 640. 60 <sup>b</sup>	131, 655. 34
$6_{51} - 5_{50}$	5		131, 655. 34

<sup>a</sup> Although the accuracy of the absolute frequencies of these lines are the same as the other lines in this Table, the splitting was measured ten times to improve the accuracy in the observed separation

$$\Delta_{K=2}(\text{splitting}) = 0.724 \pm 0.016 \text{ Mc/sec.}$$

<sup>b</sup> The quadrupole structure was not resolved because of the extremely small intensity of this absorption peak. It is possible that the recorded frequency is that of a weak vibrational satellite.

ments were made between 80 000 and 190 000 Mc/sec (1.6–3.8 mm). All the observed absorption peaks were due to *a*-type, *R*-branch transitions with  $\Delta J = +1$ ,  $\Delta K_{-1} = 0$ ,  $\Delta K_1 = +1$ .  $K_{-1}$  is referred to as *K* hereafter.

#### A. HNCO, DNCO

The observed and calculated frequencies for the  $J = 4 \leftarrow 3$ ,  $5 \leftarrow 4$  and  $6 \leftarrow 5$  transitions of HNCO are shown in Table I and for the  $J = 4 \leftarrow 3$ ,  $5 \leftarrow 4$  and  $7 \leftarrow 6$  transitions of DNCO in Table II.

For each molecule the  $K = 0, 1,$  and  $2$  lines are easily identified by their greater intensity since the unusually large  $A_0$  values lead in each case to a sharp decrease in population for successive  $K$ -states. Thus as  $K$  increases the observed transition intensity falls off rapidly (see Figs. 1-3). For each of the two molecules the  $K = 1$  lines are widely split in the manner characteristic of a slightly asymmetric top and in each transition the  $K = 2$  lines appear as a closely spaced doublet. The remaining lines in each  $K$ -pattern are not split by the asymmetry but may be identified by their positions, intensities, and temperature coefficients of intensity. The lines corresponding to  $K = 4$  show quadrupole splitting which gives further confirmation of correct assignment.

TABLE II  
FREQUENCIES OF DNCO LINES FROM MOLECULES IN THE  
GROUND VIBRATIONAL STATE

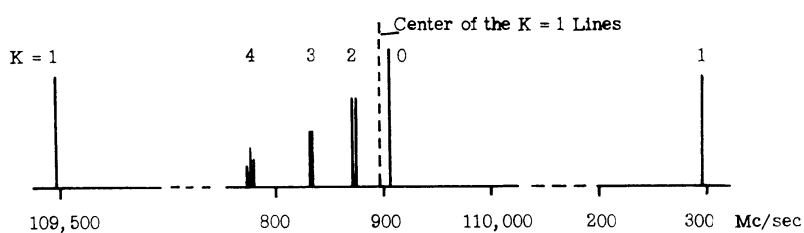
Transition	K	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)
<u>J = 4 ← 3</u>			
$4_{04} - 3_{03}$	0	81,571.53	81,571.58
$4_{13} - 3_{12}$	1	82,042.23	82,041.91
$4_{14} - 3_{13}$	1	81,106.32	81,106.13
$4_{23} - 3_{22}$	2	81,578.97	82,579.01
$4_{22} - 3_{21}$	2	81,579.61	81,579.79
$4_{32} - 3_{31}$ } $4_{31} - 3_{30}$ }	3 3	81,586.95 <sup>a</sup>	{ 81,585.58 81,585.58
<u>J = 5 ← 4</u>			
$5_{05} - 4_{04}$	0	101,963.49	101,963.36
$5_{15} - 4_{14}$	1	101,382.24	101,382.01
$5_{14} - 4_{13}$	1	102,551.73	102,551.72
$5_{24} - 4_{23}$	2	101,973.63	101,973.24
$5_{23} - 4_{22}$	2	101,975.19	101,974.81
$5_{33} - 4_{32}$ } $5_{32} - 4_{31}$ }	3 3	101,981.97 <sup>a</sup>	{ 101,981.75 101,981.75
$5_{42} - 4_{41}$ } $5_{41} - 4_{40}$ }	4 4	101,988.27 <sup>a</sup>	{ 101,988.25 101,988.25

TABLE II (continued)  
 FREQUENCIES OF DNCO LINES FROM MOLECULES IN THE  
 GROUND VIBRATIONAL STATE

Transition	K	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)
<u>J = 7 ← 6</u>			
$7_{07} - 6_{06}$	0	142,744.44	142,744.53
$7_{17} - 6_{16}$	1	141,932.08	141,932.39
$7_{16} - 6_{15}$	1	143,569.77	143,569.99
$7_{26} - 6_{25}$	2	142,760.57	142,760.57
$7_{25} - 6_{24}$	2	142,764.97	142,764.95
$7_{35} - 6_{34}$	3	142,773.02	142,773.63
$7_{34} - 6_{33}$	3		142,773.63
$7_{44} - 6_{43}$	4	142,782.23	142,783.30
$7_{43} - 6_{42}$	4		142,783.30
$7_{53} - 6_{52}$	5	142,785.65	142,784.64
$7_{52} - 6_{51}$	5		142,784.64

<sup>a</sup> Unresolved doublets or triplets due to quadrupole effects of the N<sup>14</sup> nucleus.

HNCO J = 5 ← 4



DNCO J = 5 ← 4

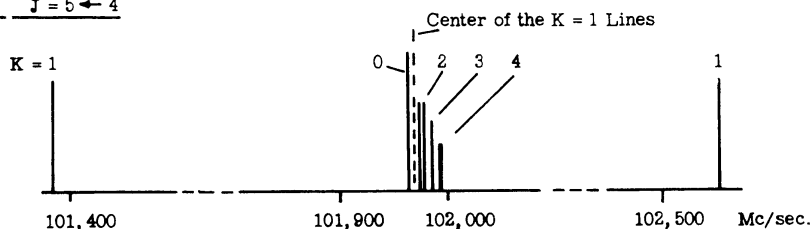


FIG. 1. The  $J = 5 \leftarrow 4$  transition, ground vibrational state, of HNCO and DNCO, showing the reversal of the  $K$ -pattern.

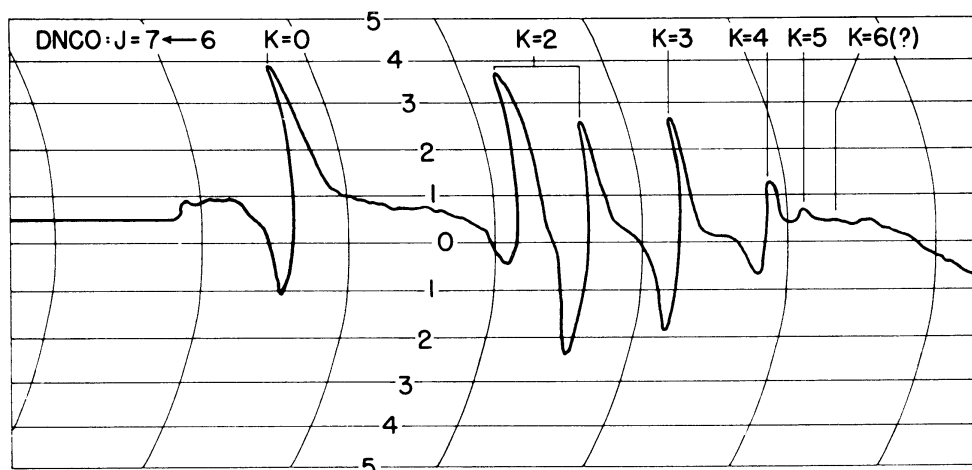
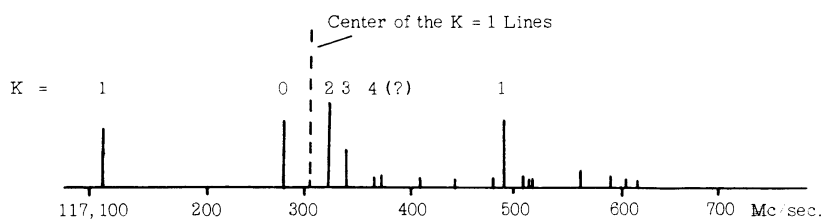


FIG. 2. Recorder trace of the central region of the  $J = 7 \leftarrow 6$  transition of DNCO. The figure shows clearly the asymmetry splitting of the  $K = 2$  line and also the rapid decrease of intensity with increasing  $K$ . The widely spaced  $K = 1$  components are not shown. The frequencies of the  $K = 0$  line is 142 744.44 Mc/sec and that of the  $K = 5$  line, 142 785.65 Mc/sec. See also Table II.

HNCS  $J = 10 \leftarrow 9$



DNCS  $J = 10 \leftarrow 9$

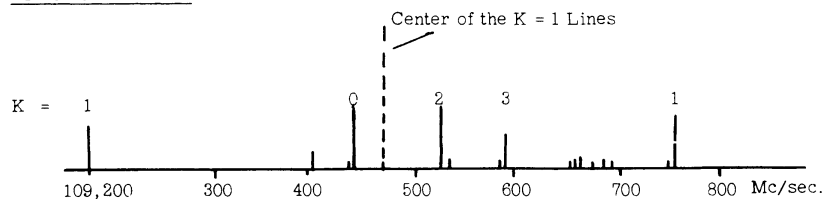


FIG. 3. The  $J = 10 \leftarrow 9$  transition of HNCS and DNCS showing in each case the strong lines  $K = 0, 1, 2, 3$ , ground vibrational state, and also the positions and relative intensities of the vibrational satellites. See Tables III, IV, X, and XI.

### B. HNCS, DNCS

The observed and calculated frequencies for the  $J = 8 \leftarrow 7, 9 \leftarrow 8, 10 \leftarrow 9$  and  $J = 16 \leftarrow 15$  transitions of HNCS and the  $J = 8 \leftarrow 7, 9 \leftarrow 8$  and  $10 \leftarrow 9$  of DNCS are given in Tables III-V. The lines with  $K = 2$  are observed to be



split only in the transitions  $J = 16 \leftarrow 15$  of HNCS and  $J = 9 \leftarrow 8$ , and  $10 \leftarrow 9$  of DNCS. The identification was done in a similar way to HNCO and DNCO except that quadrupole splitting was not resolvable. For HNCS the line with  $K = 4$  could not be distinguished with certainty from the large number of weak vibrational satellites and the  $K = 5$  line is expected to be too weak to be observed. Both  $K = 4$  and  $K = 5$  lines should be clearly observable for DNCS, but since the frequency of neither line can, at present, be accurately predicted, they again cannot be easily separated from vibrational satellites.

## IV. CENTRIFUGAL DISTORTION

The four molecules HNCO, DNCO, DNCS, and HNCS form an interesting sequence with respect to centrifugal distortion:

TABLE III  
FREQUENCIES OF HNCS LINES FROM MOLECULES IN THE  
GROUND VIBRATIONAL STATE.

Transition	K	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)
<u><math>J = 8 \leftarrow 7</math></u>			
$8_{08} - 7_{07}$	0	93,829.91	93,829.91
$8_{17} - 7_{16}$	1	93,994.96	93,995.07
$8_{18} - 7_{17}$	1	93,692.76	93,692.65
$8_{26} - 7_{25}$ } $8_{27} - 7_{26}$ }	2 2	93,863.28	{ 93,863.31 93,863.25
$8_{35} - 7_{34}$ } $8_{36} - 7_{35}$ }	3 3		{ 93,875.42 93,875.42
<u><math>J = 9 \leftarrow 8</math></u>			
$9_{09} - 8_{08}$	0	105,558.08	105,557.91
$9_{18} - 8_{17}$	1	105,743.77	105,743.74
$9_{19} - 8_{18}$	1	105,403.63	105,403.52
$9_{27} - 8_{26}$ } $9_{28} - 8_{27}$ }	2 2	105,595.61	{ 105,595.52 105,595.43
$9_{36} - 8_{35}$ } $9_{37} - 8_{36}$ }	3 3		105,609.18

TABLE III (continued)  
 FREQUENCIES OF HNCS LINES FROM MOLECULES IN THE  
 GROUND VIBRATIONAL STATE.

Transition	K	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)
<u>J = 10 ← 9</u>			
$10_{010} - 9_{009}$	0	117,285.45	117,285.66
$10_{19} - 9_{18}$	1	117,491.95	117,492.13
$10_{110} - 9_{19}$	1	117,114.04	117,114.12
$10_{28} - 9_{27}$ } $10_{29} - 9_{28}$ }	2 2	117,327.47	{ 117,327.49 117,327.37
$10_{37} - 9_{36}$ } $10_{38} - 9_{37}$ }	3 3		{ 117,342.60 117,342.60
<u>J = 16 ← 15</u>			
$16_{016} - 15_{015}$	0	187,645.15	187,645.07
$16_{115} - 15_{114}$	1	187,976.13	187,975.67
$16_{116} - 15_{115}$	1	187,370.57	187,370.84
$16_{214} - 15_{213}$	2	187,712.225 <sup>a</sup>	187,712.56
$16_{215} - 15_{214}$	2	187,711.730 <sup>a</sup>	187,712.06
$16_{313} - 15_{312}$ } $16_{314} - 15_{313}$ }	3 3	187,736.68	{ 187,736.51 187,736.51

<sup>a</sup> Although the accuracy of the absolute frequencies of these lines are the same as the other lines in this Table, the splitting was measured ten times to improve the accuracy in the observed separation

$$\Delta_{K=2} (\text{splitting}) = 0.495 \pm 0.055 \text{ Mc/sec.}$$

### A. HNCO

The calculated frequencies for HNCO in Table I were obtained using the formula

$$\begin{aligned} \nu = & (B_0 + C_0)(J + 1) + [A_0 - \frac{1}{2}(B_0 + C_0)](b_p \Delta c_1 + b_p^2 \Delta c_2 + \dots) \\ & - 4D_J(J + 1)^3 - 2D_{JK}K^2(J + 1) \\ & + 4H_{JJ}K^2(J + 1)^3 + 2H_{JK}K(J + 1)K^4 \\ & + \text{quadrupole correction terms for higher } K\text{-components.} \end{aligned} \quad (1)$$

The formula of Costain (5) is adopted and small, independent corrections for

TABLE IV  
 FREQUENCIES OF HNCS<sup>34</sup> LINES FROM MOLECULES IN THE  
 GROUND VIBRATIONAL STATE

Transition	K	Observed frequency <sup>a</sup> (Mc/sec)
<u>J = 8 ← 7</u>		
$8_{08} - 7_{07}$	0	91,625.9
$8_{17} - 7_{16}$	1	91,784.3
$8_{18} - 7_{17}$	1	91,495.6
$8_{26} - 7_{25}$	2	91,658.7
$8_{27} - 7_{26}$	2	
$8_{35} - 7_{34}$	3	91,671.7
$8_{36} - 7_{35}$	3	

<sup>a</sup> An insufficient number of transitions have been measured for an appropriate formula to be found which will fit the observations.

$D_J$  is assumed to be the same as for HNCS<sup>32</sup>.

the quadrupole effects and the slight asymmetry are made. The  $H_{JJJ}$  term is omitted as it is too small to give an observable effect within the present experimental accuracy. Both  $D_J$  and  $D_{JK}$  have positive signs and  $H_{JKK}$ ,  $H_{JJK}$ , and  $D_J$  are small compared with  $D_{JK}$ . The expression gives a fit to all lines except  $K = 5$  in the  $J = 6 \leftarrow 5$  transition. This is a weak line and it is possible either that the recorded frequency is that of a vibrational satellite or that higher order terms are needed in Eq. (1) to fit higher  $K$ -values. The  $K$ -pattern for the  $J = 5 \leftarrow 4$  transition, ground vibrational state is shown in upper part of Fig. 1.

## B. DNCO

For DNCO an interesting and unexpected change in the characteristic  $K$ -pattern is found. The components  $K = 2, 3, \dots$  and the center frequency of the  $K = 1$  lines all lie on the high-frequency side of  $K = 0$  in sharp contrast to the situation in HNCO. Also the spacing of the lines is considerably less. The  $J = 5 \leftarrow 4$  transition of DNCO is shown in the lower part of Fig. 1. Figure 2 shows a recorder trace of the central part of the  $J = 7 \leftarrow 6$  transition in DNCO, i.e., excluding the widely spaced  $K = 1$  lines. The line with  $K = 6$  although observed could not be measured due to its very small intensity.

The observed frequencies can be well fitted to Eq. (1) with a root-mean-

square deviation of 0.4 Mc/sec (see Table II). The rather large errors for higher values of  $K$  are due to difficulties in making accurate measurements because of unresolved quadrupole structure and the weakness of these lines. It is seen from Table VI that  $D_{JK}$  changes sign from HNCO to DNCO.  $D_J$  for DNCO is, as usual, positive and constant for all  $K$ -components within the experimental accuracy.

### C. DNCS

The  $K$ -splitting for DNCS is much larger than for any of the other three molecules as can be seen from Figs. 1 and 3. The semiempirical formulas used for the calculated frequencies are

$$\begin{aligned}
 K = 0 & \quad \nu = (10\,945.763)(J + 1) - 4D_J(J + 1)^3, \\
 K = 1 & \quad \nu = (10\,948.169 \pm 27.624)(J + 1) - 4D_J(J + 1)^3, \\
 K = 2 & \quad \nu = (10\,953.640)(J + 1) - 4D_J(J + 1)^3, \\
 K = 3 & \quad \nu = (10\,960.247)(J + 1) - 4D_J(J + 1)^3,
 \end{aligned} \tag{2}$$

TABLE V  
FREQUENCIES OF DNCS LINES FROM MOLECULES IN THE  
GROUND VIBRATIONAL STATE

Transition	K	Observed frequency ( Mc/sec)	Calculated frequency (Mc/sec)
Previous measurements (3)			
<u>J = 2 ← 1</u>			
$2_{02} - 1_{01}$	0	21,891.66	21,891.49
$2_{11} - 1_{10}$	1	21,951.82	21,951.59
$2_{12} - 1_{11}$	1	21,841.04	21,841.05
Present measurements			
<u>J = 8 ← 7</u>			
$8_{08} - 7_{07}$	0	87,563.05	87,563.34
$8_{17} - 7_{16}$	1	87,803.28	87,803.79
$8_{18} - 7_{17}$	1	87,361.71	87,361.81
$8_{26} - 7_{25}$	2	87,626.37	87,626.86
$8_{27} - 7_{26}$	2		87,626.59
$8_{35} - 7_{34}$	3	87,679.66	87,679.53
$8_{36} - 7_{35}$	3		87,679.53

TABLE V (continued)  
 FREQUENCIES OF DNCS LINES FROM MOLECULES IN THE  
 GROUND VIBRATIONAL STATE

Transition	K	Observed frequency (Mc/sec)	Calculated frequency (Mc/sec)
<u>J = 9 ← 8</u>			
${}^9_{09} - {}^8_{08}$	0	98,507.94	98,507.93
${}^9_{18} - {}^8_{17}$	1	98,778.22	98,778.50
${}^9_{19} - {}^8_{18}$	1	98,281.15	98,281.27
${}^9_{27} - {}^8_{26}$	2	98,579.41	98,579.54
${}^9_{28} - {}^8_{27}$	2	98,578.99	98,579.14
${}^9_{36} - {}^8_{35}$	3	98,638.64	98,638.72
${}^9_{37} - {}^8_{36}$	3		98,638.72
<u>J = 10 ← 9</u>			
${}^{10}_{010} - {}^9_{09}$	0	109,452.06	109,452.23
${}^{10}_{19} - {}^9_{18}$	1	109,752.49	109,752.93
${}^{10}_{110} - {}^9_{19}$	1	109,200.75	109,200.45
${}^{10}_{28} - {}^9_{27}$	2	109,532.36	109,531.98
${}^{10}_{29} - {}^9_{28}$	2	109,531.83	109,531.45
${}^{10}_{37} - {}^9_{36}$	3	109,597.60	109,597.67
${}^{10}_{38} - {}^9_{37}$	3		109,597.67

and were obtained by least square analysis. The exact way in which the term multiplying  $(J + 1)$  varies with  $K$  is not yet understood.  $D_J$  has the same value for all values of  $K$  within the experimental accuracy, and the very small asymmetry correction term

$$[A_0 - \frac{1}{2}(B_0 + C_0)](\Delta c_2 b_p^2)$$

must be added in each case. The observed frequencies can also be fitted roughly by Eq. (1) giving an rms error of 0.8 Mc/sec with  $D_{JK} = -1.125$  Mc/sec;  $H_{JKK} = -36.19$  Kc/sec;  $H_{JJJ} = H_{JJK} = 0$ . The deviation is outside the estimated experimental error and, furthermore, if Eq. (1) is then used to predict the  $K = 4$  line of DNCS then the calculated frequency is 109 624.92 in the  $J = 10 \leftarrow 9$  transition which is not within 30 Mc/sec of any observed line. Even though this  $K = 4$  line is expected to be quite strong, about 1/2.5 of the intensity

of the  $K = 3$  peak, identification has not yet been possible. The  $J = 10 \leftarrow 9$  transition including vibrational satellites, Fig. 3, illustrates this difficulty.  $D_{JK}$  is negative as for DNCO and  $D_J$  positive.

#### D. HNCS

The observed frequencies are found to give least square fits to the formulas:

$$\begin{aligned}
 K = 0 & \quad \nu = (11\,729.046)(J + 1) - 4D_J(J + 1)^3, \\
 K = 1 & \quad \nu = (11\,730.784 \pm 18.901)(J + 1) - 4D_J(J + 1)^3, \\
 K = 2 & \quad \nu = (11\,733.207)(J + 1) - 4D_J(J + 1)^3, \\
 K = 3 & \quad \nu = (11\,734.726)(J + 1)^3 - 4D_J(J + 1)^3 \\
 & \quad + [A_0 - \frac{1}{2}(B_0 + C_0)]\Delta c_2 b_p^2 \text{ asymmetry correction in each case.}
 \end{aligned} \tag{3}$$

Although the spacing of the  $K$ -pattern is smaller than for DNCS (see Fig. 3) an attempt to fit to Eq. (1) gives the large rms error of 1.95 Mc/sec for the  $K = 0, 1, 2$ , and 3 lines. Also the  $K = 4$  frequency predicted by (1) would be 117 290.37 Mc/sec for  $J = 10 \leftarrow 9$ , which was not among the observed frequencies. The  $K = 0, 1, 2$ , and 3 frequencies can of course be fitted by adding a term of the type  $(J + 1)K^6$  to Eq. (1), but here again no agreement between the predicted  $K = 4$  frequency, 117 548.37 Mc/sec, and observation is found. It is doubtful whether such a term is justified theoretically. The way in which the centrifugal distortion  $K$ -pattern changes does not appear to be directly related to the order of increasing asymmetry, HNCS—DNCS—HNCO—DNCO. Very little change in the  $K$ -pattern takes place when  $S^{34}$  is substituted for  $S^{32}$  in HNCS.

Assuming that both high and low frequency  $K = 1$  components are equally shifted by centrifugal stretching we can calculate  $(B_0 - C_0)$  from the  $K = 1$  splitting  $(B_0 - C_0)(J + 1)$ ,  $(B_0 + C_0)$  from  $K = 0$  frequencies and  $D_J$ , and  $A_0$  from the  $K = 2$  splitting. All rotational and centrifugal distortion constants are shown in Table VI.

#### V. QUADRUPOLE EFFECTS

No quadrupole splitting was noticed in the spectrum of either HNCS or DNCS because of the low  $K$  and high  $J$  values involved. Quadrupole structure on the  $K = 3$  and  $K = 4$  lines of HNCO gives a value of  $eqQ = +2.0 \pm 0.2$  Mc/sec for the  $N^{14}$  nucleus in good agreement with the previous value of  $2.00 \pm 0.05$  Mc/sec which was obtained from measurements on the  $K = 0$  line in the  $J = 1 \leftarrow 0$  of HNCO (6). Furthermore, analysis of the quadrupole interaction shows that a weak line in the  $J = 5 \leftarrow 4$  and  $6 \leftarrow 5$  transitions of HNCO which at first was thought to be a component of the split  $K = 4$  line is, in fact, a vibrational satellite.

TABLE VI  
SPECTROSCOPIC CONSTANTS OF HNCO, DNCO, HNCS AND DNCS.

Spectroscopic Constants	HNCO	DNCO	HNCS	DNCS	HNCS <sup>34</sup>
$(B_0 + C_0)$ Mc/sec	$21,981.602 \pm 0.050$	$20,393.28 \pm 0.050$	$11,729.046 \pm 0.015$	$10,945.763 \pm 0.058$	$11,453.54 \pm 0.20$
$(B_0 - C_0)$ Mc/sec	$160.438 \pm 0.050$	$233.944 \pm 0.050$	$37.802 \pm 0.024$	$55.248 \pm 0.082$	$36.08 \pm 0.20$
$B_0$ Mc/sec	$11,071.020 \pm 0.050$	$10,313.612 \pm 0.050$	$5,883.424 \pm 0.015$	$5,500.506 \pm 0.050$	$5,744.81 \pm 0.20$
$C_0$ Mc/sec	$10,910.582 \pm 0.050$	$10,079.668 \pm 0.050$	$5,845.622 \pm 0.015$	$5,445.257 \pm 0.050$	$5,708.73 \pm 0.20$
$A_0$ Mc/sec	$956,400 \pm 50,000$	$534,500 \pm 70,000$	$1,483,000 \pm 167,000$	$723,400 \pm 25,000$	--
$I_b^{\circ}$ amu $A^2$	$45.66255 \pm 0.00025$	$49.0159 \pm 0.00025$	$85.92462 \pm 0.00022$	$91.90627 \pm 0.00085$	$87.9979 \pm 0.0035$
$I_c^{\circ}$ amu $A^2$	$46.334009 \pm 0.00025$	$50.1535 \pm 0.00025$	$86.48027 \pm 0.00022$	$92.83878 \pm 0.00085$	$88.5540 \pm 0.0035$
$I_a^{\circ}$ amu $A^2$	$0.5286 \pm 0.0290$	$0.9458 \pm 0.1260$	$0.3409 \pm 0.0389$	$0.6988 \pm 0.0250$	--
$\delta_{I_c^{\circ} - I_a^{\circ} - I_b^{\circ}}$ amu $A^2$	$0.1429$	$0.1918$	$0.2148$	$0.2337$	--
$b_p \times 10^5$	$-8.485$	$-22.31$	$-1.280$	$-3.848$	--
$\chi$	$-0.99966$	$-0.99911$	$-0.99995$	$-0.99985$	--
$D_J$ Kc/sec	$3.55 \pm 0.5$	$2.95 \pm 0.5$	$1.17 \pm 0.05$	$1.22 \pm 0.31^a$	--
$D_{JK}$ Kc/sec	$837.0$	$-227.1$	--	--	--
$H_{JKK}$ Kc/sec	$-0.056$	$0.147$	--	--	--
$H_{JKK}$ Kc/sec	$2.81$	$-5.61$	--	--	--

<sup>a</sup> It was necessary to use the observations on the  $J = 2 \leftarrow 1$  transition of DNCS (3) to determine  $D_J$  with fair accuracy.

## VI. MOLECULAR STRUCTURE

The molecular structure previously given for HNCS (3) was one for which the structural parameters were chosen to fit the observed rotational constants  $\frac{1}{2}(B + C)$  and  $2(B - C)$  for the  $K = 1$  state for the species HNCS<sup>32</sup>, HNCS<sup>34</sup>, DNCS<sup>32</sup>, HNC<sup>13</sup>S, and DNC<sup>13</sup>S to 0.25 Mc/sec or better. The inaccuracy inherent in this treatment is discussed below. However the earlier structure can legitimately be used to calculate for HNC<sup>13</sup>S in the  $K = 1$  state the quantity  $(B - C)$ , which was not reported. Taking this calculated value with the observed mean frequency of the  $2_{12} - 1_{11}$  and  $2_{11} - 1_{10}$  transitions for this molecule (2) and making the justifiable assumption that the change in the  $D_{JK}$  term from HNCS to HNC<sup>13</sup>S is smaller than the experimental error then a more accurate and reliable structure calculation is possible. The structure obtained is insensitive to the above assumptions but it does rely on the further, and less sure, assumption that both  $K = 1$  components for a transition of a particular species are equally affected by centrifugal distortion.

The procedure is as follows:

(i) Use of Kraitchman's equations (7) for a planar asymmetric rotor to determine the  $y_s$  and  $z_s$  coordinates of the hydrogen atom relative to principal axes of HNCS.

(ii) Determination of the  $z_s$  coordinates of carbon and sulfur. The  $y_s$  coordinates of C and S cannot be determined in this way because of the proximity of these atoms to the principal  $z$ -axis.

(iii) Use of the first moment equation

$$\sum_i m_i z_{si} = 0$$

to give the nitrogen  $z$ -coordinate.

(iv) Determination of structural parameters from equations

$$\begin{aligned} \sum_i m_i y_i &= 0, \\ \sum_i m_i y_i z_i &= 0, \end{aligned}$$

using the geometrical relations between  $y$  and  $z$  coordinates of the four atoms and assuming the linearity of the —N—C—S chain.

In (i) and (ii) the moments of inertia  $I_b^0$  and  $I_c^0$  were used since these are measured with much greater accuracy than  $I_a^0$ .

This leads to the molecular structure given in Table VII where the errors contain estimated contributions due to the method of calculation used in addition to the experimental error.

The N—C and C—S distances are very close to those previously given but the discrepancies for the H—N—C angle ( $4^\circ 44'$ ) and N—H distance (0.024 Å) are unusually big. These differences are a result of using different methods of computation and rotational constants. The earlier treatment (3) includes in the



TABLE VII  
STRUCTURAL PARAMETERS FOR HNCS

New values	Previous (3)
$r(\text{N}-\text{C}) = 1.216_4 \pm 0.007 \text{ \AA.}$	1.216 \text{ \AA.}
$r(\text{N}-\text{H}) = 0.988_7 \pm 0.003 \text{ \AA.}$	1.013 \text{ \AA.}
$r(\text{C}-\text{S}) = 1.560_5 \pm 0.003 \text{ \AA.}$	1.561 \text{ \AA.}
$\angle \text{H-N-C} = 134^\circ 59' \pm 10'$	$130^\circ 15'$

structural parameters the alteration in the centrifugal distortion constants between HNCS and DNCS, particularly the  $D_{JK}$  term, which leads to the above-mentioned errors. An approximate calculation shows that  $\angle \text{HNC}$  can only alter by about  $1^\circ$  between the  $K = 0$  and  $K = 3$  states due to rotation about the  $a$ -axis and the change from  $K = 0$  and  $K = 1$  states would be much less. Also the earlier structure was obtained by a least squares ' $r_0$ ' treatment whereas the present one is found mostly by the more reliable ' $r_s$ ' method. The new structure is therefore not expected to reproduce the observed rotational constants  $A_0$ ,  $B_0$ , and  $C_0$ , and quite a large difference between the calculated and observed  $I_a$  may be expected for HNCS since  $I_a^0$  was not used in the calculation of the present parameters.

For HNCO there is still insufficient data to give an improved structure over that given earlier (1). Observations on higher transitions of the species  $\text{HN}^{15}\text{CO}$  and  $\text{HNCO}^{18}$  would be required to give an improved set of parameters. In view of the similarity of the molecular structures of HNCO and HNCS and also the frequencies of the N—H stretching vibration,  $3531 \text{ cm}^{-1}$  in HNCO (8) and  $3536 \text{ cm}^{-1}$  in HNCS (9), it is very likely that the N—H distance is almost the same in each molecule.

#### VII. MOLECULES IN EXCITED VIBRATIONAL STATES

The presence of a light off-axis atom in each of these molecules will, in addition to modifying the rotational spectrum of the ground vibrational state from that of a linear triatomic molecule, also remove the degeneracy of the two heavy-atom bending vibrations which is present in molecules of the OCS type. For each of HNCO, DNCO, HNCS, and DNCS it is therefore expected that two sets of much weaker lines will be present, in addition to those dealt with in Sections III and IV, due to molecules in the vibrational states  $v_5 = 1$  and  $v_6 = 1$ . The frequencies for the low-lying vibrational states and the appropriate Boltzmann factors are shown in Table VIII.  $\nu_5$  is the frequency of the NCS or NCO in plane bend, and  $\nu_6$  is the frequency of the NCS or NCO out of plane bend.

TABLE VIII  
BOLTZMANN FACTORS FOR THE  $\nu_4 = 1$ ,  $\nu_5 = 1$  AND  $\nu_6 = 1$  STATES

Vibrations	HNCO		HNCS		DNCS	
	Infrared frequency $\text{cm}^{-1}$ (8)	Boltzmann factor	Infrared frequency $\text{cm}^{-1}$ (9)	Boltzmann factor	Infrared frequency $\text{cm}^{-1}$	Boltzmann factor
$\nu_4$	798	1/45	817	1/50	580 <sup>a</sup>	1/17
$\nu_5$	572	1/16	469	1/10	b	b
$\nu_6$	670	1/25	600	1/18	b	b

<sup>a</sup> Estimated from  $\nu_4$  of HNCS.

<sup>b</sup> Vibration frequencies and Boltzmann factors for  $\nu_5 = 1$  and  $\nu_6 = 1$  may be assumed to be approximately the same as for HNCS.

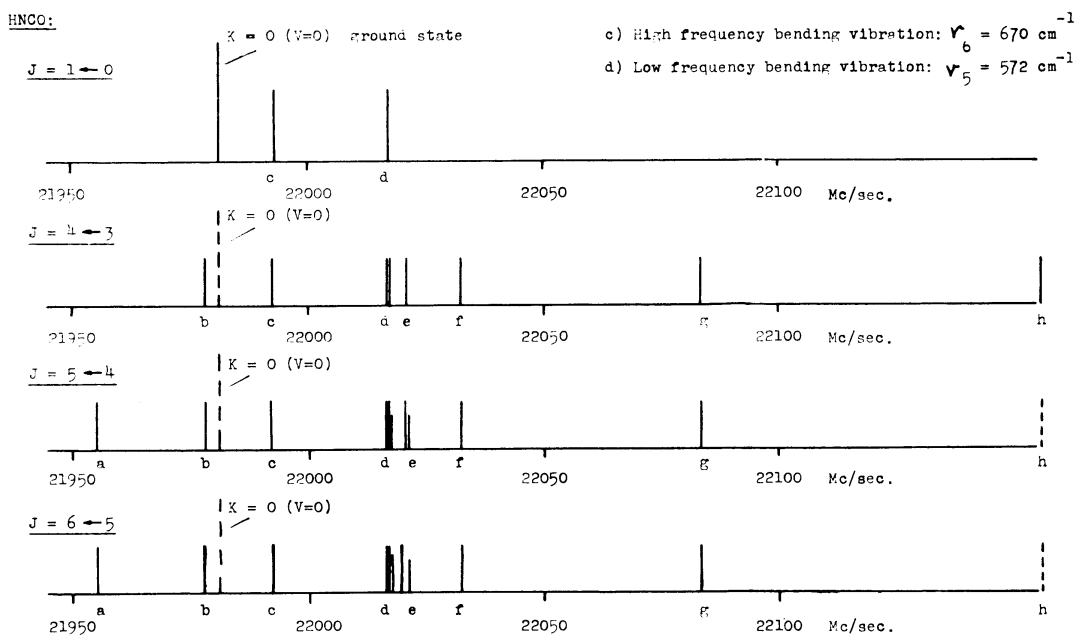


FIG. 4. Rotational transitions of HNCO molecules in the vibrationally states  $\nu_5 = 1$  and  $\nu_6 = 1$ . The frequency scale is  $\nu/(J + 1)$ ; see Table IX. The difference in behavior of lines *c* and *d* with increasing *J* is illustrated here. The  $J = 1 \leftarrow 0$  transition is taken from Reference 1.

In addition the vibration  $\nu_4$ , the H—N—C angle bend, which occurs at  $798 \text{ cm}^{-1}$  for HNCO and  $817 \text{ cm}^{-1}$  for HNCS would be expected to occur at lower frequency for the deuterated compounds where  $\nu_4^{(D)} \approx 1/\sqrt{2} \nu_4^{(H)}$  or approximately  $560 \text{ cm}^{-1}$  and  $580 \text{ cm}^{-1}$  for DNCO and DNCS, respectively. The present

TABLE IX  
 VIBRATIONAL SATELLITES FOR HNC0 FROM  $v_5 = 1$  AND  $v_6 = 1$  STATES.

Transition J = 4 ← 3			Transition J = 5 ← 4			Transition J = 6 ← 5		
Line	Observed frequency (Mc/sec)	$\frac{v}{(J+1)}$	Line	Observed frequency (Mc/sec)	$\frac{v}{(J+1)}$	Line	Observed frequency	$\frac{v}{(J+1)}$
			a	109, 776.42	21, 955.28	a	131, 730.84	21, 955.14
b	87, 913.08	21, 978.27	b	109, 890.69	21, 978.14	b	131, 868.33	21, 978.06
c	87, 969.72	21, 992.43	c	109, 958.67	21, 991.73	c	131, 952.11	21, 992.01
d	88, 067.49	22, 016.87	d	110, 083.80	22, 016.76	d	132, 099.82	22, 016.64
d'	88, 069.80	22, 017.45	d'	110, 086.08	22, 017.22	d'	132, 102.88	22, 017.15
e	88, 083.84	22, 020.96	d''	110, 089.41	22, 017.88	d''	132, 106.60	22, 017.77
f	88, 131.78	22, 032.95	e	110, 104.11	22, 020.82	e	132, 115.04	22, 019.17
g	88, 334.64	22, 083.66	e'	110, 105.52	22, 021.10	e'	132, 125.44	22, 020.91
h	88, 623.90	22, 155.98	f	110, 164.08	22, 032.82	f	132, 195.68	22, 032.61
			g	110, 419.08	22, 083.82	g	132, 500.92	22, 083.49

observations on vibrationally excited molecules cover HNCS, DNCS, and HNCO. The concentration of DNCO in the prepared sample was not sufficient for the frequencies of the vibrational satellites to be measured.

### A. HNCO

For HNCO the earlier observations (6) reveal two lines in the  $J = 1 \leftarrow 0$  transition which were assigned to rotational transitions of molecules in the  $v_5 = 1$  and  $v_6 = 1$  states (see Fig. 4 and Table IX). The present measurements show corresponding lines in the three newly observed transitions, except that the line *c* from the  $v_6 = 1$  state (out of plane NCO bend) consistently appears as a single line whereas the  $v_5 = 1$  vibrational satellite (in-plane bend) *d* is successively split as the value of  $J$  increases (see Fig. 4). Also widely spaced lines *a* and *g* approximately centered on the frequency of the lines *d* are seen and these may be reasonably assigned to  $v_5 = 1, K = 1$ . The line *f* could be

TABLE X  
VIBRATIONAL SATELLITES FOR HNCS FROM  $v_5=1$  AND  $v_6=1$  STATES

J = 8 ← 7			J = 9 ← 8		
Line	Observed frequency (Mc/sec)	$\frac{\nu}{(J+1)}$	Line	Observed frequency (Mc/sec)	$\frac{\nu}{(J+1)}$
b	94,086.9	11,760.86	b	105,847.5	11,760.83
c	94,073.3	11,759.16	c	105,831.6	11,759.07
d	94,053.4	11,756.68	d	105,810.0	11,756.67
			d'	105,802.2	11,755.80
f	94,012.2	11,751.53	f	105,765.8	11,751.76
			f'	105,764.9	11,751.66
g	94,003.9	11,750.49	g	105,756.8	11,750.76
			g'	105,749.3	11,749.92
			g''	105,748.3	11,749.81
h	93,983.7	11,747.96	h	105,730.5	11,747.83
i	93,953.3	11,744.16	i	105,698.6	11,744.29
			j	105,672.8	11,741.42
k	93,902.9	11,737.86	k	105,640.1	11,737.79
k'	93,899.3	11,737.41			
l	93,895.6 <sup>a</sup>	11,736.95	l	105,631.7 <sup>a</sup>	11,736.86
m	93,851.2	11,731.40	m	105,585.4	11,731.71
n	93,695.0	11,711.88	n	105,406.7	11,711.86

TABLE X (continued)  
 VIBRATIONAL SATELLITES FOR HNCS FROM  $v_5=1$  AND  $v_6=1$  STATES

J = 10 ← 9			J = 16 ← 15		
Line	Observed frequency (Mc/sec)	$\frac{\nu}{(J+1)}$	Line	Observed frequency (Mc/sec)	$\frac{\nu}{(J+1)}$
a	117,615.4	11,761.54	a	188,181.5	11,761.34
b	117,606.8	11,760.68			
c	117,589.8	11,758.98	c	188,131.7	11,758.23
d	117,562.5	11,756.25			
e	117,523.4	11,752.34			
f	117,516.8	11,751.68	f	188,015.4	11,750.96
			f'	188,010.9	11,750.68
g	117,506.6	11,750.66	g	188,001.0	11,750.06
h	117,479.9	11,747.99			
i	117,444.9	11,744.49			
j	117,413.8	11,741.38			
k	117,377.2	11,737.72			
k'	117,371.3	11,737.13			
l <sup>a</sup>	117,367.94	11,736.794			
m	117,315.4	11,731.54			
n	117,117.5	11,711.75			

<sup>a</sup> May be K = 4, ground vibrational state.

$K = 1, v_6 = 1$  when the other line  $K = 1, v_6 = 1$  would be calculated to fall at a  $\nu/(J+1)$  value of approximately 21 951 Mc/sec but was not, however, observed. At present an assignment of the lines *b* and *h* has not been possible but it seems clear that the group *d* and *e* are due to lines with  $K = 0, 2, 3, \dots$ ,  $v_5 = 1$ .

## B. HNCS, DNCS

The earlier measurements on HNCS showed two vibrational satellites in the  $J = 2 \leftarrow 1$  transition at 23 475 Mc/sec and 23 520 Mc/sec (2) (the transition  $2_{02} - 1_{01}$  for the ground vibrational state occurs at the frequency 23 458 Mc/sec). The purely second-order Stark effect of the 23 475 Mc/sec line indicates it to be  $K = 0$  probably of the vibrational state  $v_6 = 1$  because, as for HNCO, the higher frequency of the two bending vibrations is expected to produce the smaller shift of microwave frequency from the  $K = 0$  line, ground vibrational state.

In the  $J = 10 \leftarrow 9$  transition of HNCS the lines  $k$  and  $l$  (see Table X and Fig. 5) correspond to the 23 475 Mc/sec line at  $J = 2 \leftarrow 1$ . Lines  $k$  and  $l$ ,  $J = 10 \leftarrow 9$ , are 91.7 and 82.5 Mc/sec, respectively, to higher frequency of the ground state  $K = 0$  line. A single line appearing at a similar shift of 85.3 Mc/sec is found at 109 537.4 Mc/sec in the same transition of DNCS (see Table XI). It is therefore possible that either  $k$  or  $l$ , for HNCS, is  $K = 4$ , ground vibrational

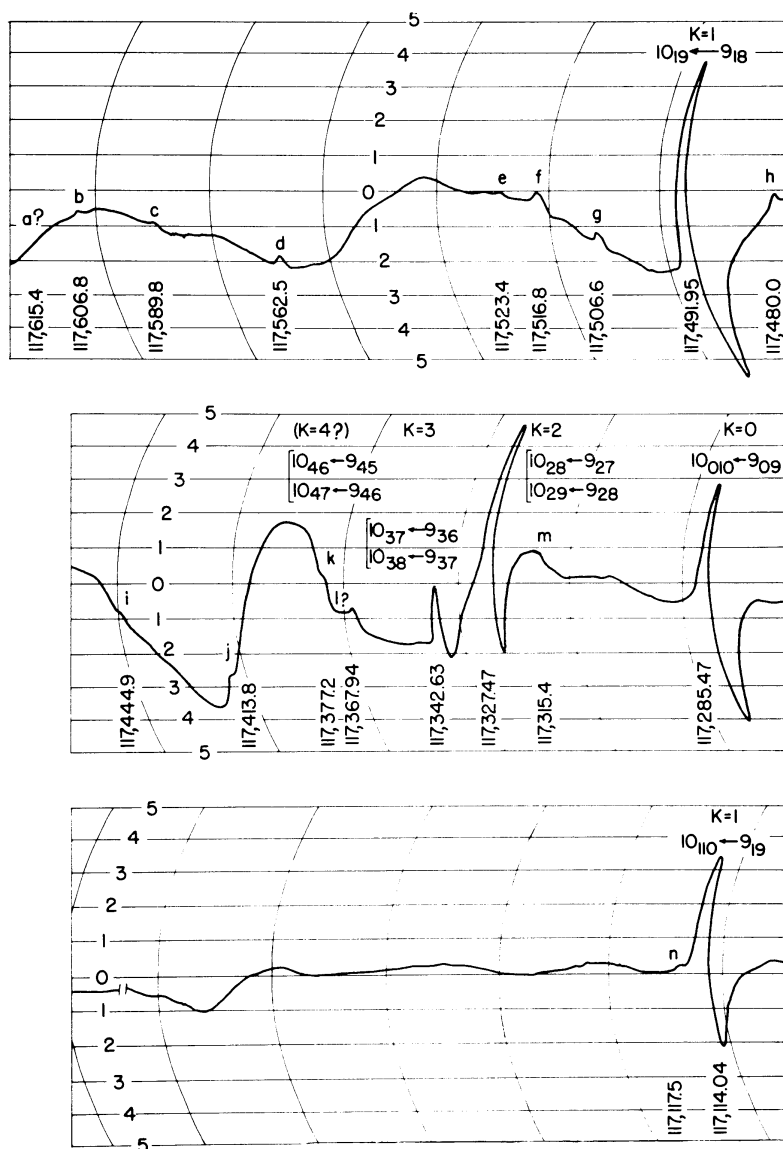


FIG. 5. Recorder trace of  $J = 10 \leftarrow 9$  transition of HNCS. The lines with  $K = 0, 1, 2, 3$ , ground vibrational state, can be clearly distinguished by their intensity. The lettered lines are vibrational satellites except that  $l$  may be  $K = 4$  ground vibrational state; see Tables III and X.

TABLE XI  
 VIBRATIONAL SATELLITES FOR DNCS PROBABLY FROM  $v_4 = 1$ ,  $v_5 = 1$  AND  $v_6 = 1$  STATES

J = 8 ← 7			J = 9 ← 8			J = 10 ← 9		
Line	Observed frequency (Mc/sec)	$\frac{\nu}{(J+1)}$	Line	Observed frequency (Mc/sec)	$\frac{\nu}{(J+1)}$	Line	Observed frequency (Mc/sec)	$\frac{\nu}{(J+1)}$
a	87, 870.4	10, 983.80	a	98, 854.3	10, 983.81	a	109, 837.2	10, 983.72
b	87, 799.3	10, 974.91	b	98, 773.9	10, 974.88	b	109, 748.5	10, 974.85
c	87, 777.1	10, 972.14				c	109, 721.4	10, 972.14
e	87, 742.8	10, 967.85	e	98, 710.2	10, 967.80	d	109, 710.6	10, 971.06
f	87, 734.2	10, 966.78	f	98, 701.6	10, 966.84	e	109, 679.3	10, 967.93
g	87, 730.7	10, 966.34	g	98, 697.6	10, 966.40	f	109, 667.4	10, 966.74
						g	109, 664.5	10, 966.45
						h	109, 663.2	10, 966.32
						i	109, 656.9	10, 965.69
j	87, 671.8	10, 958.98	i	98, 691.0	10, 965.67	j	109, 588.8	10, 958.88
k	87, 631.1	10, 953.89	j	98, 628.9	10, 958.77	k	109, 537.4	10, 953.74
l	87, 555.0	10, 944.38	k	98, 584.5	10, 953.83	l	109, 445.9	10, 944.59
m	87, 531.0	10, 941.38	l	98, 504.1	10, 944.90	m	109, 413.3	10, 941.33
			m	98, 472.6	10, 941.40			
			m'	98, 440.8	10, 937.87	n	109, 239.9	10, 923.99

state. Deuteration will normally reduce a vibration-rotation interaction constant,  $\alpha$ , so that a likely interpretation is that  $k$  for HNCS with 91.7 Mc/sec shift and  $k$  for DNCS with 85.3 Mc/sec shift are  $K = 0$  lines of the vibrational state  $v_6 = 1$  for each molecule. It appears possible that the 23 520 Mc/sec line,  $J = 2 \leftarrow 1$ , with a reported first-order Stark effect (2) may be  $K = 1$  ( $2_{11} - 1_{10}$ ) of the  $v_6 = 1$  state. This corresponds to line  $c$ , 117 589.8 Mc/sec,  $J = 10 \leftarrow 9$  so the small line at 117 117.5 Mc/sec, close to the low-frequency  $K = 1$  line ground vibrational state, may be  $10_{110} - 9_{19}$ ,  $v_6 = 1$ . However, the mid frequency of lines  $c$  and  $n$  is 117 353.6 Mc/sec, 24 Mc/sec below  $k$ , whereas the center frequency of the  $K = 1$  components exceeds the  $K = 0$  line frequency by 17.45 Mc/sec in the ground vibrational state. The groups  $e, f, g$  for HNCS and  $e$  through  $i$  for DNCS since they each occur at about the same frequency shift from their respective  $K = 0$  lines, ground vibrational state, are likely to be the  $K = 0, 2, 3$  lines for the other vibration  $v_5$ , but the  $K = 1$  lines for this vibrational state have so far not been assigned. The line  $m$  at 109 413.3 Mc/sec,  $J = 10 \leftarrow 9$ , or DNCS, may be one such line or it could be due to the vibrational state  $v_4 = 1$  which should be sufficiently populated to give observable lines (see Table VIII). The frequencies of some observable vibrational satellites have not been recorded on account of the experimental difficulty of measuring the weakest lines.

#### VIII. DISCUSSION OF CENTRIFUGAL DISTORTION

It can be seen from Table VI that for each of the molecules studied the degree of asymmetry (shown by the value of  $\kappa$  or  $b_p$ ) is very small and, in fact, these molecules were expected to exhibit, very closely, symmetric top behavior. For such small asymmetry the asymmetric top centrifugal distortion formula (10)

$$W = W_0 + A_1 W_0^2 + A_2 W_0 J(J+1) + A_3 J^2(J+1)^2 + A_4 J(J+1)(P_z^2)_{av} + A_5 (P_z^4)_{av} + A_6 W_0 (P_z^2)_{av} \quad (4)$$

should simplify to give an expression very similar to Eq. (5), in which  $(B_0 + C_0)$  replaces  $2B_0$  in the symmetric top expression and small asymmetry and quadrupole corrections are included:

$$\nu = (B_0 + C_0)(J+1) - 4D_J(J+1)^3 - 2D_{JK}K^2(J+1) + \text{asymmetry and quadrupole terms.} \quad (5)$$

Similarly the treatment developed by Baker (11) to explain the observed mm-wave spectrum of formyl fluoride, HCOF, seems also to reduce to the same equation when the asymmetry is as small as for HNCO, DNCO, HNCS, and DNCS.

The nonexistence of intense vibrational satellites for any of the four molecules indicates that the infrared assignment of  $817 \text{ cm}^{-1}$  to the H—N—C angle bend-



ing mode (8) is correct and hence that no vibration with frequency lower than  $\nu_5$  is taking place. Therefore since no low-lying vibrational state or inversion barrier is present, theory similar to that used by Lide (12), for  $\text{NH}_2\text{CN}$ , will not be applicable.

For HNCS the energy for rotation about the molecular  $a$ -axis for  $K = 3, 4 \dots$  will be of similar magnitude to energies of the vibrations  $\nu_4$ ,  $\nu_5$ , and  $\nu_6$ . For example the  $a$ -axis rotational energy is near  $440 \text{ cm}^{-1}$  for  $K = 3$ , HNCS ( $\nu_5 = 469 \text{ cm}^{-1}$ ). The displacement to lower frequencies for  $K = 3$  is very noticeable in the observed spectrum (Fig. 3).

The work of Wilson (13) shows that in the harmonic limit interaction between two vibrational states can only occur when each of two quantum numbers for those vibrational states differ by one unit, e.g., states  $v_1 = 1, v_2 = 0$ , and  $v_1 = 0, v_2 = 1$  can interact. Such a condition clearly cannot be satisfied if one of the states is the ground vibrational state with all  $v_i = 0$ . However, considerable anharmonicity may be present in the vibrations of HNCS particularly for  $\nu_4$  in which the amplitude of the  $\angle\text{HNC}$  bending vibration is estimated as  $+11^\circ, -15^\circ$  (3) about the equilibrium position ( $\angle = 136^\circ$ ) for the ground vibrational state,  $\frac{1}{2}h\nu_4$ .

It also seems likely that the usual asymmetric rotor centrifugal distortion expression Eq. (4) which is derived strictly by first-order perturbation theory would not be adequate when high rotational energies and an anharmonic vibration of large amplitude are involved.

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