The Structure and Dipole Moment of Isothiocyanic Acid

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The Structure and Dipole Moment of Isothiocyanic Acid *

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"Thiocyanic acid" in the vapor state has been found to be at least 95 percent HNCS. From an analysis of the microwave rotational spectrum the following bond distances and bond angle were determined $rH-N = 1.01A$ (assumed), $rN-C = 1.218A$, $rC-S = 1.557A$, H−N−C angle 136°. Analysis of the Stark spectrum indicates that the component of dipole moment along the molecular figure axis is 1.72 D. Stark components from transitions forbidden in the zero-field spectrum have been observed.

I. INTRODUCTION

CONFLICTING physical evidence concerning the nature of the valence bonds in the thiocyanates and the ratio of the equilibrium concentration of the two tautomeric forms of thiocyanic acid have lent the problem of the structure of these compounds considerable interest. The study of the microwave spectrum of CH_3NCS, which is complicated by the presence of internal rotating groups in the molecule, has also made it desirable to know the detailed structure of the NCS group in order to expedite the spectral analysis. The study of the microwave spectrum of the thiocyanic acids and the Stark effect in that spectrum, reported in this paper, was undertaken to help settle these questions. The structures of the molecules having observable spectra were obtained and it was also found possible to determine a component of the dipole moment from a quantitative analysis of the Stark effect. The Stark patterns of the microwave spectra permit the application of the detailed Stark effect theory to the class of slightly asymmetric molecules.

II. PREPARATION OF THE ACID

Rück and Steinmetz[1] suggest two methods of preparation for "thiocyanic acid." Both methods were used to some extent in this investigation. In the first method potassium thiocyanate and $KHSO_4$ crystals were pulverized, dried under vacuum, mixed thoroughly, and heated gently to speed up the reaction and drive the acid vapor into the wave-guide absorption cell. A modification of the second method, although requiring a short drying tube, made possible a convenient synthesis of the deuterium derivatives. D_2O and P_2O_5 were mixed to give D_3PO_4 to which KSCN was added. The mixture was then gently warmed to liberate the "thiocyanic acid." $KSC^{13}N$ was prepared by fusing sulfur with KCN containing 17 percent of C^{13}. It was then used in the preparation of $HNC^{13}S$ and $DNC^{13}S$.

Thiocyanic acid, which is said in the literature to be a tautomeric mixture of HSCN and HNCS, is a crystalline solid stable below 0°C and polymerizing at ordinary temperatures to a yellow insoluble compound. At high temperatures organic thiocyanates rearrange to give isothiocyanates. Two points of chemical interest were noted in this investigation; first, only isothiocyanic acid seemed to be present in the dilute samples of vapor admitted to the wave-guide absorption cell and second, the polymerization could be reversed to some extent by strong heating to liberate monomeric HNCS.

III. OBSERVED SPECTRUM

The microwave absorption spectrum of the isothiocyanic acid vapor was observed over the frequency range from 20,000 to 25,000 Mc using a Stark modulation microwave spectrometer. Square-wave modulation was used with the lower voltage at zero volts and with the higher voltage set at values from 4 to 160 v. The electrode separation within the wave guide was such as to make these voltages correspond to fields of from 20 to 800 v/cm. The observed zero-field spectrum and Stark patterns at the highest value of the field and at one intermediate value are shown in Fig. 1. Qualitative
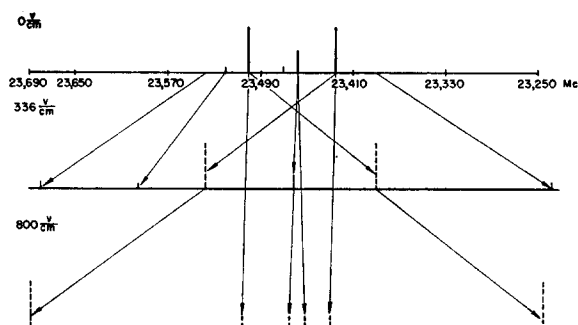

Fig. 1. Observed spectra.

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[1] V. Rück and H. Steinmetz, Zeits. f. Anorg. Chemie **77**, 51 (1912).

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studies of the observed intensities and their variations with temperature seem to indicate that the two weakest lines in the zero-field spectrum correspond to rotational transitions of molecules in excited vibrational states. The remaining pattern, presumably due to rotational transitions of molecules in the ground state of vibration, consists of five lines, two of which could not actually be seen at zero field and whose frequencies have been fixed by extrapolation. Of the three visible zero-field lines two possessed both first-order and second-order Stark components while the center line possessed two second-order Stark components. These simple qualitative features of the Stark spectrum indicate immediately
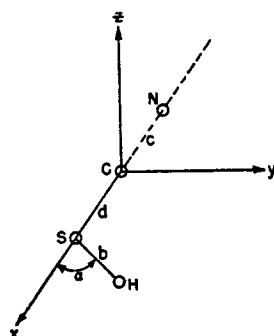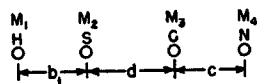

FIG. 2. HSCN coordinates.

that the molecule is not linear (because of the presence of the first-order Stark components) but has nearly the structure of a symmetric rotor. Furthermore, the presence of two Stark components for each line (corresponding to $M^2=0$ and $M^2=1$) indicates that the transition involves $J=1$. The small asymmetry indicated for the molecule suggests that we are dealing with a linear NCS or SCN group[2] with the H bonded at an angle giving a close approach to a prolate symmetric-rotor. In such a case the transition would have to be $J=1 \rightarrow J=2$. For a slightly asymmetric rotor three $J=1 \rightarrow J=2$ transitions are possible

$$1_{1,1;0} \rightarrow 2_{1,2;-1}$$
$$1_{0,1;-1} \rightarrow 2_{0,2;-2}$$
$$1_{1,0;+1} \rightarrow 2_{1,1;0}.$$
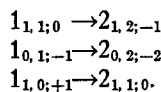
In the symmetric-rotor approximation the first and third of these would possess both second-order and first-order Stark components while the second transition would have only second-order components.

A detailed discussion of the Stark patterns for these transitions, based on the accurate asymmetric-rotor treatment, is presented in another section. This discussion confirms the above qualitative conclusions and

serves to determine a value for the dipole moment of the molecule.

IV. ROTATIONAL CONSTANTS

From the observed frequencies of the three lines corresponding to the above transitions, values of two of the rotational constants for the molecule in the ground vibrational state may be obtained. These frequencies and the others given in Table I were measured to an accuracy of ± 1 Mc by the method of Good and Coles.[3]

From the observed frequencies for the $1_{1,1;0} \rightarrow 2_{1,2;-1}$ and $1_{1,0;+1} \rightarrow 2_{1,1;0}$ transitions it is possible to calculate values of the two nearly degenerate rotational constants B and C if the following approximation is made. Following Wang[4] the energy of a molecule which is nearly a prolate symmetric-rotor may be written

$$F(J, K) = \tfrac{1}{2}(B+C)J(J+1) + [A - \tfrac{1}{2}(B+C)]K^2,$$

so that for a $\Delta J=1$, $\Delta K=0$ transition the frequency would be

$$\nu = (B+C)(J+1)$$

where J is the lower of the two values of the principal rotational quantum number. This frequency would be approximately the average of the two observed frequencies. The average of the measured frequencies is 23,462 Mc and the corresponding value of $\tfrac{1}{2}(B+C)$ is 5865.5 Mc.

If the equation given by King, Hainer, and Cross[5] for the rotational energy levels of an asymmetric rotor,

$$E_T{}^J(a, b, c) = [\tfrac{1}{2}(a+c)]J(J+1) + [\tfrac{1}{2}(a-c)]E_r{}^J(K),$$

is used, together with the exact expressions for $E_r{}^J(K)$ tabulated in their paper the result may easily be derived that the difference in frequency of the two transitions $1_{1,1;0} \rightarrow 2_{1,2;-1}$ and $1_{1,0;+1} \rightarrow 2_{1,1;0}$ is equal to $(A-C)(K+1)$ or simply to $2(C-B)$. The observed frequency difference is 75 Mc so that $(C-B)$ is 37.5 Mc. The derived values of B and C together with the calculated moments of inertia are $B=5903$ Mc, $C=5728$ Mc, $I_B=142.1 \times 10^{-40}$ gcm^2, $I_C=143.96 \times 10^{-40}$ gcm^2. The

TABLE I. Observed spectrum of HNCS.

Transition	Molecule	νMc	
$1_{1,1;2} \rightarrow 2_{1,2;-1}$	HNCS	23,499.5	
$1_{1,0;+1} \rightarrow 2_{1,1;0}$	HNCS	23,424.5	
$1_{1,1;0} \rightarrow 2_{1,1;0}$	HNCS	23,537	(Extrapolated)
$1_{1,0;+1} \rightarrow 2_{1,2;-1}$	HNCS	23,387	(Extrapolated)
$1_{0,1;-1} \rightarrow 2_{0,2;-2}$	HNCS	23,458	
⋯	HNCS	23,475	(Weak)
⋯	HNCS	23,520	(Weak)
$\tfrac{1}{2}[\nu(1_0 \rightarrow 2_{-1}) + \nu(1_{+1} \rightarrow 2_0)]$	HNC^{13}S	23,389	
$\tfrac{1}{2}[\nu(1_0 \rightarrow 2_{-1}) + \nu(1_{+1} \rightarrow 2_0)]$	HNCS^{34}	22,915	
$\tfrac{1}{2}[\nu(1_0 \rightarrow 2_{-1}) + \nu(1_{+1} \rightarrow 2_0)]$	DNCS	21,897	
$\tfrac{1}{2}[\nu(1_0 \rightarrow 2_{-1}) + \nu(1_{+1} \rightarrow 2_0)]$	DNC^{13}S	21,839	

[2] X-ray analysis in 1934 showed the (SCN)$^-$ ion was linear [M. Strada, Gazz. 64, 400 (1934)].

[3] W. E. Good and D. K. Coles, Phys. Rev. 71, 383 (1947).
[4] S. C. Wang, Phys. Rev. 34, 243 (1929).
[5] King, Hainer, and Cross, J. Chem. Phys. 11, 27–42 (1943).

most probable structure of thiocyanic acid is a planar one and for a rigid planar molecule the relation

$$I_C = I_A + I_B$$

must be satisfied. If the molecule is treated as a rigid one a value of $I_A = 1.83 \times 10^{-40}$ gcm^2 is obtained with $A = 459,000$ Mc. However, since the molecule was actually in the ground vibrational state and therefore not truly planar these last two values are merely rough approximations.

Less complete spectral patterns were obtained for the isotopic molecules so that only approximate values of $\frac{1}{2}(B+C)$ were obtained. The frequencies corresponding to these rotational constants were the superposition points of the two "non-forbidden" first-order Stark components. The identification of the majority of these lines as corresponding to the indicated isotopic molecule rests upon a very pronounced increase in intensity for samples of the acid vapor made from materials enriched in the appropriate isotopes. The line ascribed to HNC^{12}S^{34}, however, was observed in a non-enriched sample and its identification depends on the molecular structure derived from the other data, to some extent.

V. CALCULATION OF INTERNUCLEAR DISTANCES

The initial calculation of internuclear distances was based on the assumption that the molecule giving rise to the observed spectrum was HSCN, thiocyanic acid. This seemed reasonable since the acid was prepared from KSCN. Furthermore Sidgwick,[6] for example, states that of the two alternative structures $H-S-C \equiv N$ and $H-N=C=S$, the former is the more probable.

If in calculating the internuclear distances and bond angles the molecule is treated as an asymmetric one, the method of Hirschfelder[7] may be used. Labeling the molecular coordinates as in Fig. 2 the following relations are obtained:

$$I_x = m_H b^2 \sin^2\alpha - (1/M)[m_H b \sin\alpha]^2$$
$$I_y = [m_S d^2 + m_N C^2 + m_H (d+b \cos\alpha)^2]$$
$$\quad - (1/M)[m_S d - m_N C + m_H (d+b \cos\alpha)]^2$$
$$I_z = [m_S d^2 + m_N C^2 + m_H (b^2 + d^2 + 2bd \cos\alpha)]$$
$$\quad - (1/M)[m_H b \sin\alpha]^2$$
$$\quad - (1/M)[m_S d - m_N C + m_H (d+b \cos\alpha)]^2$$
$$I_{xy} = m_H (d+b \cos\alpha) b \sin\alpha$$
$$\quad - (1/M)[m_H b \sin\alpha][m_S d - m_N C + m_H (d+b \cos\alpha)]$$
$$I_{xz} = I_{yz} = 0.$$

From these quantities the three principal moments of inertia I_A, I_B, and I_C may be found using the equations:

$$I_A = \frac{1}{2}(I_x + I_y) - \frac{1}{2}[(I_x + I_y)^2 - 4(I_x I_y - I_{xy}^2)]^{\frac{1}{2}}$$
$$I_B = \frac{1}{2}(I_x + I_y) + \frac{1}{2}[(I_x + I_y)^2 - 4(I_x I_y - I_{xy}^2)]^{\frac{1}{2}}$$
$$I_C = I_z.$$

If complete sets of rotational constants were available

for all of the isotopic molecules it would be formally possible to solve for the three interatomic distances and the one angle. In view of the obvious complications involved several simplifying approximations were made.

Since it is obvious from the observed spectrum that the effect of the H atom on the moments of inertia is small the molecule may be treated approximately as a linear molecule where the fictitious $H-S$ distance along the SCN axis might be thought of as an "effective projection" of the actual $H-S$ distance in space (Fig. 2). For a linear molecule the equation for I_C about an axis through the center of gravity can be written as:

$$I_C = (1/M)[m_1 m_2 l_{12}^2 + m_1 m_3 l_{13}^2 + m_1 m_4 l_{14}^2 + m_2 m_3 l_{23}^2 + m_2 m_4 l_{24}^2 + m_3 m_4 l_{34}^2]$$

where the l's are the distances between atoms of the same subscripts. When the l's are expressed in terms of b_1, d, and c with accurate values of atomic masses, four equations, one for each of the isotopic molecules, are obtained. The additional approximation is made that $\frac{1}{2}(B+C) \simeq C$ linear. A graphical solution of these equations resulted in the values

$$H-S = 1.55A, \quad C-N = 1.33A, \quad \text{and} \quad S-C = 1.47A.$$

The $C-N$ and $S-C$ distances are probably less in error than the $H-S$ projection since they are less sensitive to changes in the symmetry of the molecule. If these two values are taken together with the value for the $H-S$ distance, 1.35A, which is the observed distance in H_2S, it should be possible using the equations for I_C and the observed value of that quantity to calculate α, the bond angle. However, at this point it becomes obvious that no real solution to this equation is possible for the given set of constants. This suggests strongly that the assumed order of atoms in the molecule is incorrect. Furthermore, as is shown in Table II the $S-C$ and $C-N$ distances fall quite outside the limits set from an examination of the force-constant data by Goubeau and Gott[8] and Linnett and Thompson.[9] Goubeau and Gott, moreover, as a result of their

TABLE II.

Bond	HSCN calculated distances	Goubeau and Gott distances	Linnett and Thompson distances	HNCS calculated distances
A. Internuclear distances in the thiocyanates				
C−N	1.33A	1.21A	1.17–1.22A	
S−C	1.47	1.69	1.60–1.67	
N−C		1.21		1.21A
C−S		1.56		1.57
B. Bond distances calculated as sum of Pauling covalent radii				
C≡1X	C=N	C−N	H−N
1.15A	1.27A	1.47A	1.00A
S≡C	S=C	S−C	H−S
1.47A	1.61A	1.81A	1.34A

[6] N. V. Sidgwick, The Organic Chemistry of Nitrogen (Oxford University Press, London, 1937).
[7] J. O. Hirschfelder, J. Chem. Phys. 8, 431L (1940).

[8] J. Goubeau and O. Gott, Ber. 73B, 127 (1940).
[9] J. W. Linnett and H. W. Thompson, J. Chem. Soc. 1399–1403 (1937).

examination of the vibrational spectrum of thiocyanic acid and other thiocyanates conclude that HNCS is the predominant form of the acid. Gallais and Voight[10] from measurements of molecular magnetic rotations also conclude that the molecule is isothiocyanic acid.

If the above procedure is repeated for HNCS the results of the graphical solution of the four linear equations are: "H−N"=0.76A, N−C=1.21, and C−S =1.57. The accurate equation for I_C is

$$I_C = I_z = [m_s d^2 + m_N C^2 + m_H(b^2 + c^2 + 2bc \cos\alpha)]$$
$$- (1/M)[m_H b \sin\alpha]^2$$
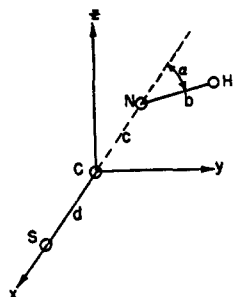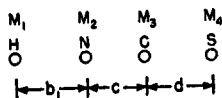$$- (1/M)[m_s d - m_N C - m_H(c + b \cos\alpha)]^2$$

FIG. 3. HNCS coordinates. Structural parameters: $a=44°$, $b=1.01A$ (assumed), $c=1.218A$, $d=1.557A$.

and for I_y

$$I_y = [m_s d^2 + m_N C^2 + m_H(c + b \cos\alpha)^2]$$
$$- (1/M)[m_s d - m_N C - m_H(c + b \cos\alpha)]^2.$$

If the following equation is used, which is a somewhat better approximation than the linear one

$$\tfrac{1}{2}(I_y + I_z) \cong 2(J+1)(h/8\pi^2 c)/\nu \text{ cm}^{-1}$$

slightly more accurate values of the internuclear distances are obtained, namely: N−C=1.218A, C−S =1.557A. If these two distances together with the H−N distance 1.01A observed in the NH_3 molecule are substituted in the equation for I_z and the experimental value of that quantity is used, a value for the H−N−C angle of 136° results. While this value of the angle is only approximate, because of the lack of sensitivity of the observed moment, the resulting set of structural parameters gives an accurately calculated spectrum which agrees with the observed one to within the accuracy claimed for the structural data (±0.01A and ±5°). The final structure for isothiocyanic acid obtained in this investigation is shown in Fig. 3. The N−C and C−S distances are seen in Table II to be in good agreement with the data of Goubeau and Gott. Since only one set of spectral lines was observed it would appear

as a result of this investigation that the equilibrium concentration of HSCN in a mixture of the two thiocyanic acids is less than five percent of the concentration of HNCS.

VI. STARK SPECTRUM AND DIPOLE MOMENT

The rotational energy levels of a rigid slightly asymmetric rotor in the presence of a homogeneous electric field have been treated by Penney.[11] The Stark effect calculations presented here have been carried out using the method of Golden and Wilson[12] and, though somewhat more elaborate, account for the observed Stark spectrum in greater detail.

The diagonal elements of the energy matrix H are given by

$$H_{J\tau M} = W_{J\tau}^0 + E^2 \sum_{J',\tau',g}' \frac{\mu_g^2[(\Phi_{Zg})_{J,\tau,M;J',\tau',M}]^2}{(W_{J\tau}^0 - W_{J'\tau'}^0)},$$

neglecting polarization terms, or

$$H_{J\tau M} = W_{J\tau}^0 + \sum_g [W_g^{(2)}]_{J\tau M},$$

where

$$W_{gJ\tau M}^{(2)} = \mu_g^2 E^2 \left[\frac{(J^2 - M^2)}{4J^2(4J^2-1)} \sum_\tau' \left\{ \frac{[(\Phi_{Zg})_{J,\tau;J-1,\tau'}]^2}{W_{J\tau}^0 - W_{J-1,\tau'}^0} \right\} \right.$$
$$+ \frac{M^2}{4J^2(J+1)^2} \sum_{\tau'\neq\tau}' \left\{ \frac{[(\Phi_{Zg})_{J,\tau;J,\tau'}]^2}{W_{J\tau}^0 - W_{J\tau'}^0} \right\}$$
$$\left. + \frac{(J+1)^2 - M^2}{4(J+1)^2(2J+1)(2J+3)} \sum_{\tau'}' \left\{ \frac{[(\Phi_{Zg})_{J,\tau;J+1,\tau'}]^2}{W_{J\tau}^0 - W_{J+1,\tau'}^0} \right\} \right].$$

Cross, Hainer, and King[13] have tabulated values of line strength λ defined as follows:

$$\lambda = \sum_{FMM'} |\Phi_{Fg}|^2_{J\tau M;J'\tau'M'}$$
$$= 3|\Phi_{Zg}|^2_{J,J'} X |\Phi_{Zg}|^2_{J\tau;J'\tau'} X \sum_{M,M'} |\Phi_{Zg}|^2_{J,M;J'M'}.$$

The necessary values of $[(\Phi_{Zg})_{J,\tau;J'\tau'}]^2$ were therefore calculated from the tabulated values of λ. In order to determine the Stark energy levels for $1_{1,1;0}$ and $1_{1,0;+1}$

TABLE III. Stark effect of $J=1\rightarrow2$ transition in HNCS.

$H_{10;0}$	$= W_{10} -2.16 \times 10^{-6}\mu_g^2 E^2$ Mc
$H_{10;1}$	$= W_{10} -1.62 \times 10^{-6}\mu_g^2 E^2$ Mc
$H_{1+1;0}$	$= W_{1+1} -2.155 \times 10^{-6}\mu_g^2 E^2$ Mc
$H_{1+1;0}$	$= W_{1+1} -1.616 \times 10^{-6}\mu_g^2 E^2$ Mc
$H_{1-1;0}$	$= W_{1-1} +4.324 \times 10^{-6}\mu_g^2 E^2$ Mc
$H_{20;0}$	$= W_{20} +1.246 \times 10^{-6}\mu_g^2 E^2$ Mc
$H_{20;1}$	$= W_{20} +0.814 \times 10^{-6}\mu_g^2 E^2$ Mc
$H_{2-1;0}$	$= W_{2-1} +1.235 \times 10^{-6}\mu_g^2 E^2$ Mc
$H_{2-1;1}$	$= W_{2-1} +0.930 \times 10^{-6}\mu_g^2 E^2$ Mc
$H_{2-2;0}$	$= W_{2-2} +1.026 \times 10^{-6}\mu_g^2 E^2$ Mc
$H_{1-1;1}$	$= W_{1-1} -2.881 \times 10^{-6}\mu_g^2 E^2$ Mc
$H_{2-2;1}$	$= W_{2-2} +0.52 \times 10^{-6}\mu_g^2 E^2$ Mc

[10] F. Gallais and D. Voight, Comptes Rendus 210, 104 (1940).

[11] W. G. Penney, Phil. Mag. 11, 602 (1931).
[12] S. Golden and E. B. Wilson, J. Chem. Phys. 16, 669 (1948).
[13] Cross, Hainer, and King, J. Chem. Phys. 12, 210 (1944).

TABLE IV. Stark spectrum of HNCS $\mu_0 = 1.72\ D$.

Field volts cm	$\frac{1}{2}(\nu_{1_{+1}\to 2_0}+\nu_{1_0\to 2_{-1}})$		$\nu_{1_{+1}\to 2_0}$; $M^2=1$		$\nu_{1_0\to 2_{-1}}$; $M^2=1$		$\nu_{1_0\to 2_0}$; $M^2=1$	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
800	23,467	23,469	23,249	23,247.5	23,685	23,689		
600	23,464.7	23,464.5	23,308	23,307	23,622	23,622		
400	23,463	23,465	23,369	23,371	23,557	23,560		
336	23,463	23,463.5	23,390	23,390	23,536	23,537	23,684	23,680
270	23,462.5	23,462.5	23,412.5	23,411	23,512.5	23,514	23,649	23,654
200	23,462	23,462	23,436	23,436	23,488	23,488	23,614	23,618
156	23,462	23,462	23,449	23,451	23,475	23,473	23,589	23,596
120	23,462	23,462	23,463	23,462	23,461	23,462	23,573	23,581
40	23,462	23,462	23,497	23,488	23,427	23,437	23,539	23,551
18	23,462	23,462	23,498	23,496	23,426	23,428		

and for $2_{1,2;-1}$ and $2_{1,1;0}$ which are nearly degenerate pairs of levels it was necessary to solve secular equations. Their solutions had the form

$$W = \tfrac{1}{2}(H_{J\tau M} + H_{J'\tau'M})$$
$$\pm \tfrac{1}{2}\{[H_{J\tau M} - H_{J'\tau'M}]^2 + 4|\xi^2|E^2\}^{\frac{1}{2}}.$$

For these two cases $|\xi|^2$ had the form

$$|\xi|^2 = (M^2/4J^2(J+1)^2)\mu_0^2|(\Phi_{Zg})_{J\tau, J\tau;}|^2.$$

The results of the Stark effect calculations for HNCS are given in Tables III and IV and are compared to the observed frequencies. A satisfactory fit of these data was obtained using a value of 1.72 debye units for the component of the permanent electric dipole moment along the I_A axis. The influence of the component of the dipole moment perpendicular to this axis was found to be negligible.

The originally puzzling anomaly of Stark components which did not originate in any of the lines observed in the zero-field spectrum is resolved by a consideration of the discussion of the intensity of Stark components given by Golden and Wilson.[12] A result of this discussion is the conclusion that if transitions are normally permitted between state m and state l but not between state m and state k, transitions between the latter become possible in the presence of an electric field if states k and l are degenerate. Figure 4 shows the normally permitted and forbidden transitions between the two pairs of nearly degenerate levels involved in this spectrum. The zero-field frequencies of lines A and D had to be obtained by extrapolation since the lines were completely forbidden in the absence of the field. To the accuracy of the extrapolation the theoretical relation between the frequency differences

$$B - C = [\tfrac{1}{2}(a-c)](2K+2)$$
$$A - D = [\tfrac{1}{2}(a-c)](4K+4)$$
$$A - D = 2(B-C)$$

was obeyed. The intensity of the forbidden lines was a function of the electric field, being zero at zero field, building up to a maximum at intermediate values of the field, and then declining at higher fields. Since the line broadened at the same time (due to inhomogeneities in the field) it could not be observed at values of the field above 400 v/cm. Presumably the intensity of these lines goes to zero at some high value of the field.
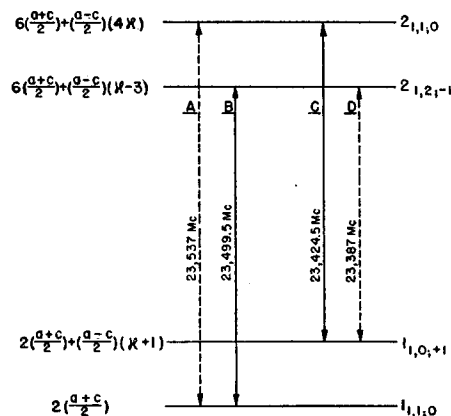

FIG. 4. Forbidden transitions.

Another point of interest in the Stark spectrum is the shift in the "center of gravity" of the first-order Stark components due the second-order terms in $H_{J\tau M}$. This shift amounted to some 6 Mc at 800 v/cm. The Stark effects for the first-order components of the forbidden and allowed transitions were simply related being the sum of terms for the former and the difference for the latter. The agreement of calculated and observed frequencies is quite good in all cases except two; the Stark effect for the first-order components of the forbidden lines and for the first-order components of the allowed lines, at the lowest values of the field. Both of these discrepancies may represent experimental error since the breadth and weakness of the components of the forbidden lines made accurate frequency measurements difficult and because "zero basing" and accurate measurement of the very low voltage square waves gave some trouble.

VII. OTHER LINES

Two other lines appeared in the observed spectrum having intensities very much less than for the lines so far identified. These probably represent transitions for molecules in excited vibrational states. It was not found possible to make accurate temperature coefficient measurements of intensity so that this hypothesis has not been adequately tested. The line at 23,520 Mc appeared to have a first-order Stark component while the line at 23,475 Mc had a purely second-order Stark effect.