Microwave Spectrum and Nonplanarity of Cyanamide

D. J. MILLEN, G. TOPPING,* AND DAVID R. LIDE, JR.[†]

William Ramsay and Ralph Forster Laboratories, University College, London, England

Microwave transitions of the isotopic species H_2NCN , HDNCN, and D_2NCN have been obtained and assigned. A number of vibrational satellites are observed in each case. The origin of these is considered, and it is concluded that the equilibrium configuration about the amino nitrogen is pyramidal and that there is a low-lying molecular "inversion" level. A vibration-rotation perturbation in the case of D_2NCN indicates that for this molecule the level is about 15 cm⁻¹ above the ground state.

I. INTRODUCTION

A number of molecular structures have been proposed for cyanamide at various times but not until recently has there been definite experimental evidence from which structural decisions can be reached. Even now that there is evidence from infrared (1) and nuclear magnetic resonance (2) studies for the form H_2NCN in the solid and liquid phase and microwave spectroscopic evidence (3) that the same structural formula applies to the gas phase, the co-existence of the form HN—CNH in small amounts cannot be excluded with certainty. A structural feature of particular interest is whether or not the configuration of the C—NH₂ group is planar or pyramidal. The interest is accentuated by the recent finding (4) for formamide of a nonplanar equilibrium configuration with a low barrier ($\sim 370 \text{ cm}^{-1}$) hindering inversion. In the present microwave study of the species H₂NCN, D₂NCN and HDNCN, the ground-state rotational constants previously reported (3) have been confirmed and numerous satellite lines of the $J = 2 \leftarrow 1$ transitions have been considered in some detail. It is concluded that these require the equilibrium configuration of the C--NH₂ group to be nonplanar, and that the inversion splitting is much larger than in ammonia but somewhat smaller than in formamide. Evidence to support this view is provided by some transitions of dideutero-cyanamide which indicate departures from rigid-rotor energies, and it is suggested that a perturbation of the type discussed by Lide (5) occurs in this case.

* Present address: National Physical Laboratory, Teddington, Middlesex, England.

[†] National Science Foundation Senior Postdoctoral Fellow 1959–60; on leave from National Bureau of Standards, Washington 25, D. C.

II. ORDINARY CYANAMIDE

Of the numerous lines which were observed in H₂NCN it is convenient to consider first those arising from the $J = 2 \leftarrow 1$ transitions. Table I lists the frequencies of a number of lines in the region 39,700–40,400 Mc/sec. They fall, according to their frequencies, into three sub-groups separated by approximately 250 Mc/sec. Relative intensities within each sub-group are indicated qualitatively. The similarity of the Stark effects exhibited by members in a given sub-group leads to the assignment of each sub-group as a vibrational ground-state transition accompanied by three vibrational satellites. The members of the central sub-group are assigned as $2_{02} \leftarrow 1_{01}$ transitions of the four vibrational states and the other two sub-groups as $2_{12} \leftarrow 1_{11}$ and $2_{11} \leftarrow 1_{10}$ transitions.

The three rotational transitions for each vibrational state give rise to nearsymmetric triplets as is to be expected for a near-symmetric rotor. The two strongest triplets in the system are represented schematically in Fig. 1. From the structure of cyanamide it can be shown that the central line of the triplet $(2_{02} \leftarrow 1_{01})$ should fall within about 0.1 Mc/sec of the mean frequency of the outer pair; this estimate is not at all sensitive to the structural parameters. Reference to Table I shows that a near-symmetric triplet of this kind is not obtained by combining the strongest lines of each sub-group; instead the strongest members of K = 1 sub-groups have to be combined with the K = 0 line at 39,991.0 Mc/sec, which is certainly weaker than the neighboring line at 39,958.2 Mc sec. Similarly the strongest line in the K = 0 sub-group has to be assigned to a vibrational state which produces only the next-to-most intense lines in the K = 1 sub-group. It appears that an alternation of statistical weights is required to account even qualitatively for the intensities. Such an alternation of statistical weights of 3 to 1 is expected for odd and even K levels for a molecule whose vibrational states transform according to a point group including the operation $C_{2^{a}}$. A molecular structure for H₂NCN having a planar equilibrium configuration would satisfy this condition and so would the separate vibrational levels associated with inversion of a molecule having a pyramidal equilibrium configuration.

FREQUENCIES" AND ROTATIONAL CONSTANTS (IN MC/SEC) FOR H ₂ NUN				
Trans.	$\tau = 0$	v = 1	<i>v</i> ′	ζ,"
$2_{1z} \leftarrow 1_{1i}$	39,725.4 (vs)	39,712.3 (s)	39,845.8 (w)	$39,820^{\rm b}$ (w)
$2_{02} \leftarrow 1_{01}$	39,991.0 (s)	$39,958.2 \ (vs)$	40,120.0 (m)	40,068.0 (w)
$2_{11} \leftarrow 1_{10}$	40,252.2 (vs)	40,203.0 (s)	40,394.2 (w)	40,315.9 (w)
B_{-}	10, 129.2	10,112.1	10, 167.1	10,141.0
ϵ	9865.8	9866.9	9892.9	9893.0

TABLE I

........

* Estimated accuracy of frequencies and rotational constants is about ± 0.5 Mc/sec.

^b This frequency is approximate only.

Th

L'estation and a second



FIG. 1. Schematic representation of near symmetric triplet structure of the $J = 2 \leftarrow 1$ transition for the v = 0 and v = 1 states of H₂NCN.

It would not be the case for a molecule having a "rigid" pyramidal configuration, i.e., if the inversion levels were not resolved. For both of the possible cases, if the vibrational levels are numbered successively $v = 0, 1, 2, \dots$, states of even v have statistical weights of 3 for odd K, and 1 for even K levels. For states of odd v, the statistical weights are reversed.

It follows that the most intense line in each of the K = 1 sub-groups is to be assigned to the vibrational ground state as in the first column of Table I. The triplet centered about the very strong line at 39,958.2 Mc/sec is then assigned to the v = 1 level, for which the K = 0 levels have statistical weights of 3. The observation of a higher intensity for this vibrational satellite than for the rotational transition belonging to the ground vibrational state implies a Boltzmann factor in excess of $\frac{1}{3}$, so that the separation $W_1 - W_0$ between the v = 0 and v = 1 levels is certainly less than 250 cm⁻¹. Approximate relative intensities of the two lines indicate $W_1 - W_0$ is unlikely to be greater than about 150 cm⁻¹, and the possibility that $W_1 - W_0 \approx 0$ is not excluded. This is too low a value to be assigned to any NCN vibrational modes; infrared (1) and Raman (6) studies have led to suggested values of 429 and 513 cm⁻¹ for the NCN bending modes. It appears therefore that the most intense transition of the $2_{02} \leftarrow 1_{01}$ series is to be assigned to the v = 1 level of the NH₂ out-of-plane wagging vibration.

The question arises as to whether or not the remaining triplets labelled v' and v'' in Table I are to be attributed to higher states (v = 2 and 3) of the NH₂ wagging mode. There are indications that they are probably not to be so assigned. The infrared spectrum of liquid cyanamide shows a band at 638 cm⁻¹, which shifts on deuteration to about 545 cm⁻¹. Davies and Jones (1) have assigned these frequencies to NH₂ and ND₂ out-of-plane wagging vibrations, respectively. Since the interval between v = 0 and v = 1 has been shown in this work to be much smaller than 638 cm⁻¹, the infrared transitions presumably terminate on the v = 2 level. These highly anharmonic spacings suggest a double minimum potential function in which the potential hump centered about the planar

configuration is smaller than in ammonia, where it is about 2000 cm⁻¹. A lower hump is in accord with stabilization by resonance between the structures H_2 —C=N and $H_2\dot{N}$ =C=N⁻. A similar resonance stabilization is associated with the low barrier to inversion in formamide.

It is reasonable therefore to think of the potential function for the NH_2 wagging vibration as a parabola centered about the planar configuration on which is superposed a small symmetric potential hump.¹ The high vibrational levels will be harmonically spaced, while the lower levels are perturbed by the potential hump. The magnitude of the harmonic spacing is determined by the reduced mass for the vibration and by the parabolic constant (we avo'd the term force constant because we are discussing the situation for very large, not infinitesimally small amplitudes). The parabolic constant for cyanamide is expected to be no less than that for ammonia; in fact, the effect of conjugation between the lone pair of electrons on the nitrogen atom and the π electrons of the C=N group will tend to oppose out-of-plane bending and so increase the parabolic constant. The smaller reduced mass in cyanamide will also tend to increase the harmonic spacing. It seems very unlikely, then, that the harmonic spacing in evanamide is appreciably less than that in ammonia, which is known to be about 475 cm^{-1} (8). Since the perturbing potential hump must increase the interval between v = 1 and v = 2 above the harmonic value, we can set a conservative lower limit of 475 cm⁻¹ for the energy difference $W_2 - W_1$.

These arguments suggest very strongly that the v = 2 level of the NH₂ wagging vibration is 500 cm^{-1} or more above the ground state; the infrared band at 638 cm^{-1} can thus be reasonably assigned as the $v = 0 \rightarrow 2$ transition of this vibrational mode. While it is difficult to make accurate measurements of relative intensities in the microwave spectrum of cyanamide, both the satellite lines v' and v'' are definitely too strong to arise from a state as high as 638 cm⁻¹. Therefore the states v' and v'' do not appear to be associated with the higher levels of the NH₂ vibration. The only reasonable possibility remaining is that they are states in which one quantum of an NCN bending vibration is excited. The lower of these bending modes has been assigned (1) as 429 cm^{-1} , which leads to qualitative agreement with the observed intensities. We shall therefore assign the satellite lines labelled v' to the state in which the NCN bending mode is singly excited but the NH_2 wagging is unexcited, while v'' is the state in which both these modes are singly excited. This particular choice is made in order to satisfy the qualitative relative intensities of the v' and v'' lines (since the NCN bending mode must belong to species B_1 or B_2 the statistical weight pattern will be reversed from that of the ground state).

This assignment for v' and v'' is also supported by the observed rotational constants. It may be seen from Table I that the changes ΔB and ΔC on going from v' to v'' are similar to the changes from v = 0 to v = 1. A similar but weaker

¹ The similar potential function for ammonia is illustrated in Townes and Schawlow (7).

pair of lines is expected for the states in which the other NCN bending mode (reported at 513 cm⁻¹) is singly excited. There are a few additional very weak lines in the neighborhood of those listed in Table I, but it has not been possible to make any assignments. All other vibrational levels (including, according to the above arguments, the levels of the NH₂ wagging vibration with v > 1) will not be sufficiently populated to give readily detectable satellites.

A number of other lines in the spectrum are assigned as Q-branch transitions between K = 1 levels as in Table II. Some of these transitions show indications of fine structure, which presumably arises from nitrogen nuclear quadrupole coupling. No such structure was resolved for R-branch transitions listed in Table I, though some of the lines had under normal conditions of observation a halfwidth approaching 5 Mc/sec, which limited the accuracy of frequency measurements to about 0.5 Mc/sec. Within this accuracy the value of B-Cobtained from Table II is in agreement with that obtained from Table I.

Numerous other lines were also observed throughout the spectrum. Their origin has not been established but it is likely that they belong to the rotational fine structure of the $v = 1 \leftarrow 0$ transition.

III. DIDEUTERO-CYANAMIDE

As in ordinary cyanamide lines belonging to $J = 2 \leftarrow 1$ transitions have been observed. The more intense of these are listed in Table III, and again relative intensities within each sub-group are indicated.

In this case, unlike that of H₂NCN, the lines do not fall into obvious sets of

Q-BRANCH TRANSITIONS FOR INCOM					
Freq. (Mc/sec)	$B - C^*$				
7384.82	263.70				
$\begin{array}{c} 9490.48\\ 9491.29\\ 9493.00\\ 9493.77 \end{array}$	263.67				
27,676.0) 27,678.6	263.59				
$egin{array}{c} 31,627.4\ 31,630.6 \end{array}$	263.57				
35,841.7 35,844.4	263.55				
	Freq. (Mc/sec) 7384.82 9490.48 9491.29 9493.00 9493.77 27,676.0 27,678.6 31,627.4 31,630.6 35,841.7 35,841.4				

	TABLE	п				
m				тт	Mar	

^a Calculated from mean frequency of pattern.

0

FREQUENCIES AND	ROTATIONAL	CONSTANTS ((in Mc	(SEC)	FOR	D ₂ NCN
-----------------	------------	-------------	--------	-------	-----	--------------------

Trans.	v = 0	v = 1
$2_{12} \leftarrow 1_{11}$	35,385.5 (s)	35,422.0 (vs)
$2_{02} \leftarrow 1_{01}$	35,797.8 (vs)	35,809.7 (s)
$2_{11} \leftarrow 1_{10}$	36,209.0 (s)	36,223.6 (vs)
В	9155.3	(B + C)/2 = 8952.4
C	8743.5	

near symmetric triplets. However, three rotational transitions can be assigned to the vibrational ground state at once without ambiguity. Statistical weight considerations show that the even K levels have a weight of 2 and the odd K levels a weight of 1 for the vibrational ground state and vice versa for the v = 4level of the ND_2 wagging mode. Thus the most intense line in the central group is clearly to be assigned as the $2_{02} \leftarrow 1_{01}$ transition of the vibrational ground state. There are two lines which form a near-symmetric triplet with this very strong central line. This assigns the lines at 35,385.5, 35,797.8, and 36,209.0 Mc/sec as in the first column of Table III. By proceeding in the same way, the argument from statistical weights leads to the conclusion that the strongest unassigned line in each of the outer groups of the triplet belongs to the vibrational state v = 1. The required assignments for $2_{12} \leftarrow 1_{11}$ and $2_{11} \leftarrow 1_{10}$ are therefore 35,422.0 and 36,223.6 Mc/sec, respectively. According to a rigid rotor energy level scheme the $2_{02} \leftarrow 1_{01}$ transition would be expected at approximately 35,823 Me/sec. No absorption line is observed at this frequency, the nearest being displaced by about 13 Mc/sec (35,809.7 Mc/sec). It appears that the levels involved in the rotational transitions of the r = 1 state are not compatible with rigid rotor energies.

The anomalous pattern in the v = 1 state can be explained by a vibrationrotation interaction of the type discussed in the preceding paper (5). It is shown there that two levels v = 0, J, K and v = 1, J, K - 1 can perturb each other strongly if they are nearly degenerate, which occurs when (2K - 1)[A - (B + C)/2] is comparable with the vibrational energy difference $W_1 - W_0$. The departure from a symmetric triplet structure in the v = 1 state could be due to a perturbation of either K = 0 or K = 1 levels. However, we can eliminate any perturbation of the v = 1, K = 0 level because a similar perturbation is not found for the v = 0, K = 1 levels. By the same reasoning, an interaction between the v = 1, K = 1 and v = 0, K = 0 levels can be excluded. We must therefore accept the only remaining possibility, a near degeneracy between the v = 1, K = 1 and v = 0, K = 2 levels. This perturbation will alter both the mean position and the separation of the K = 1 lines and thus destroy the symmetric pattern in the v = 1 state. The most likely candidate for assignment as the K = 0 transition $(2_{02} \leftarrow 1_{01})$ in the v = 1 state is the line at 35,809.7 Mc/sec. If this is correct it means that the mean frequency of the K = 1 lines has been shifted by an amount $\delta v =$ +13 Mc/sec. According to Eq. (26) of the preceding paper (5), this shift is to be identified approximately with

$$\delta\nu = + \frac{4(d_{01}^2 + 9e_{01}^2)}{W_1 - W_0 - 3[A - (B + C)/2]}$$

Although the rotational constant A has not been experimentally determined we can estimate that A - (B + C)/2 is roughly 5 cm⁻¹. The constants d_{01} and e_{01} involve integrals over the vibrational eigenfunctions of the double-minimum potential and are therefore very difficult to estimate. However, we know that perturbations of the v = 0 state, which depend upon the quantity $W_1 - W_0 - [A - (B + C)/2]$ are of the order of 1 Mc/sec or less. In order that this be consistent with the 13 Mc/sec shift in the v = 1 state, the difference $W_1 - W_0$ must be very close to 3[A - (B + C)/2], or about 15 cm⁻¹. A more detailed calculation shows that whatever the values of d_{01} and e_{01} , $W_1 - W_0$ is very likely to be in the range 15-25 cm⁻¹. The choice of any other observed line for assignment to the $2_{02} \leftarrow 1_{01}$ transition would require $W_1 - W_0$ to be even closer to 15 cm⁻¹.

If we accept this value of about 15 cm⁻¹ for the "inversion splitting" $W_1 - W_0$ in D₂NCN, an analogy with formamide suggests that $W_1 - W_0$ in H₂NCN is in the range 30–100 cm⁻¹. This estimate is not inconsistent with any other experimental evidence. The present interpretation appears to be the only feasible one, but the data are too limited for it to be regarded as final. It could be confirmed by a study of higher rotational transitions, particularly K = 2 transitions in the v = 0 state, but this involves considerable experimental difficulty.

Even if the details of the present interpretation are not entirely correct, the mere existence of a strong perturbation in the spectrum of D_2NCN proves that the interval $W_1 - W_0$ is very small. If the ND₂ wagging vibration were described by a shallow parabolic potential without a hump in the planar configuration, a very large number of low-lying levels would be expected. The failure to observe such a rich satellite spectrum shows conclusively that the equilibrium configuration of cyanamide is nonplanar.

There are in fact a number of other weak satellite $J = 2 \leftarrow 1$ lines besides those listed in Table III, but it has not been found possible to suggest an assignment analogous to that given for H₂NCN in Table I. Some of the lines fall into near symmetric triplets, but others cannot be fitted into a simple pattern. The difficulty possibly arises because some of the satellites originate from vibrational states having one quantum of the ND₂ wagging vibration, as well as one quantum of some other vibrational mode; these lines might suffer a perturbation of the type discussed above.

Trans.	v = 0	v = 1
$2_{12} \leftarrow 1_{11}$	37,375.4	37,384.7
$2_{02} \leftarrow 1_{01}$	37,723.8ª	37,723.8ª
$2_{11} \leftarrow 1_{10}$	38,069.1	38,056.8
B	9604.0	9598.2
C	9257.1	9262.2

Т	'A	B	L	\mathbf{E}	Ι	V

^a Unresolved.

TABLE V

Moments of Inertia for $v = 0$ States (and A^2)				
	H ₂ NCN	D_2NCN	HDNCN	
I_b	49.9083	55.2173	52.6375	
Γ	51.2407	57.8179	54.6101	

IV. MONODEUTERO-CYANAMIDE

The strongest members of the $J = 2 \leftarrow 1$ transitions are listed in Table IV. In this case it appears that the $2_{02} \leftarrow 1_{01}$ transitions for the v = 0 and v = 1 states have not been resolved. A single very strong central line is observed from which two symmetric triplets can be formed with the K = 1 transitions as shown in Table IV. The assignment of the same value of B + C for the v = 0 and v = 1 states is not unreasonable in view of the corresponding changes in B + C found for H₂NCN and D₂NCN; for the former the change is -16.0 and for the latter +6.0 Mc/sec. Which of the triplets belongs to the vibrational ground state is not established with certainty but relative intensities suggest the assignment in Table IV.

V. MOLECULAR MOMENTS OF INERTIA AND STRUCTURE

Only a limited amount of structural information can be obtained from the two moments I_b and I_c (Table V) which have been determined for each species. It is convenient to begin by referring the coordinates of the hydrogen atoms in H₂NCN to the principal axes of the NCN group, which have been chosen as shown in Fig. 2 (*xy* is the molecular plane of symmetry). The inertia matrix for H₂NCN is then readily obtained by following a procedure analogous to that used by Kraitchman (9):

$$egin{pmatrix} \mu y^2 + 2m_{
m H}\,z^2 & -\mu xy & 0 \ -\mu xy & I^0 + \mu x^2 + 2m_{
m H}\,z^2 & 0 \ 0 & 0 & I^0 + \mu (x^2 + y^2) \end{pmatrix}. \end{split}$$



FIG. 2. Coordinate system for cyanamide

x, y and z refer to the coordinates of the hydrogen atoms in the chosen frame, I^0 is the moment of inertia of the linear NCN group and $\mu = 2m_{\rm H}M/(M + 2m_{\rm H})$, M being the mass of the NCN group and $m_{\rm H}$ the mass of a hydrogen atom. A similar matrix is obtained for D₂NCN. By equating the root which is factorized out in each case to the observed intermediate moment, $I_b^{\rm DD}$ for H₂NCN and D₂NCN, respectively, we obtain

$$I^{0} = [(I_{b}^{\text{DD}} - \rho I_{b}^{\text{HH}})/(1 - \rho)], \text{ where}$$

$$\rho = (m_{\text{D}}/m_{\text{H}}) [(M + 2m_{\text{H}})/(M + 2m_{\text{D}})].$$

No assumption about molecular planarity is made in deriving this expression, and consequently conclusions about the NCN structure based on I^0 are not dependent on the NH₂ geometry. The value for I^0 , which is found to be 44.056 amu A^2 , does not allow a determination of unique $r_{\rm CN}$ and $r_{\rm CN'}$ distances. Pairs of $r_{\rm CN}$ and $r_{\rm CN'}$ values which are compatible with I^0 have been calculated for various assumed distances d of the carbon atom from the center of mass and are listed in Table VI.² It is seen that the nitrogen-nitrogen distance is close to 2.507A independent of structural assumptions. Since C=N distances are usually in the range 1. 155–1. 1.60. A, we may conclude that $r_{\rm CN'}$ is about 1.35 A.

By using the complete secular determinants for both H₂NCN and D₂NCN it is in principle possible (if a rigid-rotor model is valid) to determine x, y, and z, and so by finding whether or not y = 0 to decide for or against planarity. x is readily obtained as a function of y from the isolated roots which may be equated to I_b^{HH} and I_b^{DD} . But it is found that for no pair of x and y values is it possible to choose a value of z which will satisfy the 2×2 determinants for both H₂NCN and D₂NCN. Exact solutions for reasonable values of x and z require imaginary values of y. The nearest approximate solution in real values is provided by a planar structure with x = 1.752 A and y = 0, for which z is found to be 0.803 and 0.813 according to whether the value for I_c^{HH} or I_c^{DD} is satisfied. For a planar

² The shorter distance, $r_{\rm CN}$, is clearly to be associated with the C = N bond.

VALUES FOR r_{CN} and $r_{CN'}$ in Cyanamide (in A)				
d	r _{CN}	ľ _{CN} ′	ν̈́nn′	
0	1.254	1.254	2.508	
0.02	1.225	1.282	2.507	
0.04	1.196	1.311	2.507	
0.05	1.182	1.325	2.507	
0.06	1.167	1.339	2.506	
0.07	1.152	1.354	2.506	

TABLE VI

structure z is obtained directly from

$$[(I_c^{HH} - I_b^{HH})/2m_H] = [(I_c^{DD} - I_b^{DD})/2m_D] = z^2.$$

For a nonplanar structure, it can be shown that $I_c - I_b$ is given approximately bv.

$$I_{c}^{\rm HH} - I_{b}^{\rm HH} = 2m_{\rm H}z^{2} - \mu y^{2} + \{\mu^{2}x^{2}y^{2}/[I_{0} + \mu(x^{2} - y^{2})]\}.$$

From these expressions it can be shown that for a rigid structure

$$[(I_c^{\rm HH} - I_b^{\rm HH})/2m_{\rm H}] - [(I_c^{\rm DD} - I_b^{\rm DD})/2m_{\rm D}] \leq 0.$$

The observed moments lead to a positive value $(+0.016 \text{ A}^2)$ for this expression. Evidently the effect of zero-point motion is sufficiently important to prevent an estimate of the deviation from molecular planarity by the use of I_c and I_b .

VI. EXPERIMENTAL

The main features of the microwave spectrometer employed in this work have already been described (10). The sample of cyanamide was introduced to the cell through a small vacuum line which was surrounded by an oven maintained at about 50°C to achieve sufficient vapor pressure. The absorption cell, which consisted of X-band copper waveguide with a Teflon-supported Stark electrode, was heated to about 75°C by a 180-watt tape heating element, insulated by glass wool and lagged with asbestos and corrugated paper. Mica windows were fitted to the cell by O-rings. To avoid any possible effect due to decomposition, cyanamide was allowed to flow through the cell continuously.

Cyanamide was prepared from a commercial sample by first recrystallizing from a 1:2 ether-benzene mixture and then by sublimation in vacuo at about 70°C (mp 46°C). The deutero-cyanamides were prepared by exchange with deuterium oxide. Samples were found to be stable for several days if kept under vacuum at or below room temperature.

ACKNOWLEDGMENT

We are grateful to the Dept. of Scientific and Industrial Research for an award to one of us (G.T.).

Note added in proof: In a recently reported investigation of the H₂NCN spectrum [G. P. Shipulo, Optics and Spectroscopy **10**, 288 (1961)] it was concluded that cyanamide has a $C_{2\nu}$ equilibrium configuration. However, the proposed interpretation of the satellite lines is inherently unreasonable and is in conflict with the infrared results. We feel that the evidence strongly supports the interpretation presented in the present paper.

RECEIVED: May 31, 1961

REFERENCES

- 1. M. DAVIES AND W. J. JONES, Trans. Farady Soc. 54, 1454 (1958).
- 2. W. G. MOULTON AND R. A. KROMHOUT, J. Chem. Phys. 25, 34 (1956).
- 3. J. K. Tyler, L. F. THOMAS, AND J. SHERIDAN, Proc. Chem. Soc. p. 155 (1959).
- 4. C. C. COSTAIN AND J. M. DOWLING, J. Chem. Phys. 32, 158 (1960).
- 5. D. R. LIDE, JR., J. Mol. Spectroscopy 8, 142 (1962). This issue.
- 6. L. KAHOVEC AND K. W. F. KOHLRAUSCH, Z. physik. Chem. 193, 188 (1944).
- C. H. TOWNES AND A. L. SCHAWLOW, "Microwave Spectroscopy," p. 301. McGraw-Hill, New York, 1955.
- G. HERZBERG, "Infrared and Raman Spectra of Polyatomic Molecules," p. 297. Van Nostrand, Princeton, 1945.
- 9. J. KRAITCHMAN, Am. J. Phys. 21, 17 (1953).
- 10. D. J. MILLEN AND K. M. SINNOTT, J. Chem. Soc. p. 350 (1958).