

# THE VACUUM ULTRAVIOLET ABSORPTION SPECTRUM OF DIAZOMETHANE\*

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Received March 12, 1964

## ABSTRACT

Ultraviolet absorption spectra of  $\text{CH}_2\text{N}_2$  and  $\text{CD}_2\text{N}_2$  between 2000 Å and 1350 Å have been photographed. Many electronic transitions occur in this region, including a Rydberg series (first reported by Herzberg) which gives the first I.P. of diazomethane as  $8.999 \pm 0.001$  eV. Examination of a band system at 1900 Å has shown that it contains three close-lying electronic transitions, with origins within  $200 \text{ cm}^{-1}$ . Of the upper states, the two outermost,  $D$  and  $F$ , are shown by rotational analysis to be of the same symmetry species  $^1B_1$ , while the third,  $E$ , lying between them, seems to be responsible for large perturbations observed in the  $K$  structures. By inference, this third state must be  $^1B_2$ , in Coriolis interaction with the two  $^1B_1$  states. Various vibrational bands of this 1900 Å group have been assigned; among these are a number of vibrationally forbidden bands involving one and three quanta of the out-of-plane  $\text{CH}_2$  bending frequency,  $\nu_6$ . There is strong evidence that the molecule remains planar in these excited states.

## 1. INTRODUCTION

In the electronic spectrum of diazomethane there are two regions of absorption on the long-wavelength side of 2000 Å. The first, studied by Brinton and Volman (1951), is a weak system of broad diffuse bands between 3200 Å and 4300 Å, overlying a continuum, and the second is another continuum between 2600 Å and 2000 Å (Kirkbride and Norrish 1933). In the vacuum ultraviolet Herzberg (1961) has found some regions of more or less discrete absorption, together with a clear Rydberg series leading to a limit at 1378 Å. No high-resolution investigations have been reported so far.

The infrared spectrum of diazomethane is consistent with that of a planar Y-shaped molecule of  $C_{2v}$  symmetry. Moore (1963) and Moore and Pimentel (1964) have observed all nine fundamental frequencies in the infrared spectrum of  $\text{CH}_2\text{N}_2$ , but only seven of the nine for  $\text{CHDN}_2$  and  $\text{CD}_2\text{N}_2$ . Their rotational analyses of perpendicular bands for all three isotopic species have given values for the ground-state rotational constants  $A - \bar{B}$ , while values of  $\bar{B}$  and  $B - C$  are available from microwave data (Sheridan 1962; Cox, Thomas, and Sheridan 1958). The three low-lying perpendicular fundamentals of  $\text{CH}_2\text{N}_2$  are strongly coupled by rotation about the  $z$  axis (Coriolis coupling), and the bands have perturbed  $K$  structures. Moore (1963) has analyzed these and determined the coupling constants.

The numbering of the vibrations in this paper is not the same as that used in all previous papers on the infrared spectrum of diazomethane. In accordance with Mulliken's (1955) notation report, the  $b_1$  and  $b_2$  species labels have been interchanged to conform with the choice of the  $x$  axis as that perpendicular to the plane of the molecule. Thus, for example, the  $\text{CH}_2$  out-of-plane bending vibration, previously  $\nu_9$ , becomes  $\nu_6$ .

\*Issued as N.R.C. No. 7919.

## 2. EXPERIMENTAL

$\text{CH}_2\text{N}_2$  was prepared by the hydrolysis of N-nitroso-N-methylurea with a strong cold aqueous solution of KOH, and extracted into di-*n*-pentyl ether (in which the gas can be stored for several days at  $-10^\circ\text{C}$  without appreciable decomposition).  $\text{CD}_2\text{N}_2$  was prepared similarly, by the hydrolysis of N-nitroso-N-methyl-*d*<sub>3</sub>-*p*-toluenesulphonamide with a strong cold solution of KOD in  $\text{D}_2\text{O}$ . This process is slow in the absence of a polar organic solvent, but in view of the danger of exchange between the KOD and the solvent, it was found preferable to omit the solvent.

Absorption spectra of  $\text{CH}_2\text{N}_2$  and  $\text{CD}_2\text{N}_2$  at room temperature, in the region 2100 Å–1350 Å, were photographed in the third and fourth orders of a 3-meter concave-grating vacuum spectrograph. The region 1950 Å–1800 Å was also photographed at  $-77^\circ\text{C}$  in the sixth order of a 10-meter concave-grating vacuum spectrograph, the slit-width being 10 microns. Kodak SWR plates were used throughout.

For convenience in filling the absorption tubes the diazomethane was diluted with helium or argon in the ratio 100:1. The absorption paths used were 20 cm and 100 cm, and the partial pressures of diazomethane were varied between 15 microns and 1 mm Hg. In the regions studied complete absorption occurs at pressures greater than these.

Wavelength standards were provided by an iron hollow cathode.

## 3. THE 1900 Å BAND SYSTEM

The 1900 Å band system consists of three electronic transitions, whose origins lie within  $200\text{ cm}^{-1}$ . Under low resolution the system consists of an intense feature at 1900 Å, formed by the three (0, 0) bands, together with a complicated group of bands at about 1860 Å, and a few scattered bands near 1800 Å. Greater gas pressures bring up many fainter bands, especially near 1840 Å, while, at the highest pressures used, further weak bands appear to the long-wavelength side of the (0, 0) bands, in the narrow "window" between this system and the 2000–2600 Å continuum.

The three (0, 0) bands are perpendicular-type, as are the majority of the bands present, but a number of narrow bands of quite different appearance are also present. The latter all involve odd quanta of the out-of-plane  $\text{CH}_2$  bending vibration, and are parallel-type, though with unusual structures.

The three electronic transitions making up this system have been called the *D*-*X*, *E*-*X*, and *F*-*X* transitions. The region 1915–1820 Å is illustrated in Fig. 1(a).

*A. Rotational Analysis of the D-X and F-X (0, 0) Bands*

The spectrum of  $\text{CH}_2\text{N}_2$  has no discrete *J* structure. In the (0, 0) bands of the *D*-*X* and *E*-*X* transitions of  $\text{CD}_2\text{N}_2$ , however, some rotational lines can be resolved, and it is also probable that the (0, 0) band of the *F*-*X* transition of  $\text{CD}_2\text{N}_2$  is not predissociated, though no rotational lines have been resolved. The *K* structures of several perpendicular-type bands are well resolved, for both  $\text{CH}_2\text{N}_2$  and  $\text{CD}_2\text{N}_2$ , and provided the key to the understanding of the band system. The three (0, 0) bands of  $\text{CD}_2\text{N}_2$  are illustrated in Fig. 1(b).

The  $K$  structure of the  $D-X$  (0, 0) band of  $CD_2N_2$  could be analyzed making use of the intensity alternation and the individual subband intensities, without reference to the infrared rotational constants for the ground state. The band proved to be strongly red-degraded, in contrast to the  $F-X$  (0, 0) band, which can be seen from Fig. 1(b) to be almost undegraded. The subband numbering was confirmed by the assignment of the first few lines of the  $^P P$  branch of the 5-6 subband. These lines were easily identified, using the microwave value  $\bar{B}'' = 0.3234 \text{ cm}^{-1}$ , and the usual  $P$ -branch formula, and the first line could be seen to be  $P(6)$ . The  $^P P$  branch of the 3-4 subband was also analyzed, though here the first line is lost in the tail of the  $^P Q$  branch. Both subbands yield the value  $\bar{B}' - \bar{B}'' = -0.0051 \text{ cm}^{-1}$ , from which it follows that  $\bar{B}' = 0.3183 \text{ cm}^{-1}$ . The assigned lines are given in Table I.

TABLE I  
Assigned  $^P P$  lines in the  $D-X$  (0, 0) and  $E-X$  (0, 0) bands  
of  $CD_2N_2$  (in  $\text{cm}^{-1}$ )

$J''$	$D-X$ (0, 0)		$E-X$ (0, 0)	
	$\kappa' = 3 \leftarrow \kappa'' = 4$	$\kappa' = 5 \leftarrow \kappa'' = 6$	$\kappa' = 3 \leftarrow \kappa'' = 4$	$\kappa' = 5 \leftarrow \kappa'' = 6$
4	—		(52586.24)*	
5	52464.78		(585.63)	
6	464.06	52437.46	584.80	52568.32
7	463.35	436.59	584.01	567.60
8	462.64	435.93	583.40	566.90
9	461.88	435.11	582.60	566.20
10	461.10	434.34	581.81	565.40
11	460.36	433.63	581.06	564.67
12	(459.68)	432.90		
13	458.86	432.17		
14	458.03	431.36		
15	457.24	430.56		
16	456.48	(429.62)		
17	455.68	(428.98)		
18	(454.81)	428.16		
19	454.07	427.38		
20	453.30	426.65		

\*Parentheses indicate blended lines.

The band type of the  $D-X$  (0, 0) band was easily determined. Qualitatively, when  $\bar{B}' = \bar{B}''$ , the  $Q$  branches of 1-0 and 0-1 subbands are shaded towards each other in a Type C band, and away from each other in a Type B band; in this case the small, but finite,  $\Delta\bar{B}$  alters the pattern, but the  $Q$  branch of the 0-1 subband is much sharper than that of the 1-0 subband, indicating Type C selection rules.

Trial spectra for the six subbands involving levels with  $K = 0, 1$ , and 2 were calculated, using the observed  $A' - \bar{B}'$ ,  $A'' - \bar{B}''$ , and  $\bar{B}' - \bar{B}''$ , and the microwave values of  $B'' + C''$  and  $B'' - C''$  (assuming a planar upper state) for both Type B and Type C selection rules. The Type C trial spectrum agrees with the observed spectrum extremely closely (incidentally explaining the peculiar  $Q$ -branch envelopes of the 2-1, 0-1, and 1-2 subbands illustrated in Fig. 1, in terms of asymmetry doubling); the Type B trial spectrum disagrees in many respects. The electronic state  $D$  is thus of symmetry  $B_1$ .

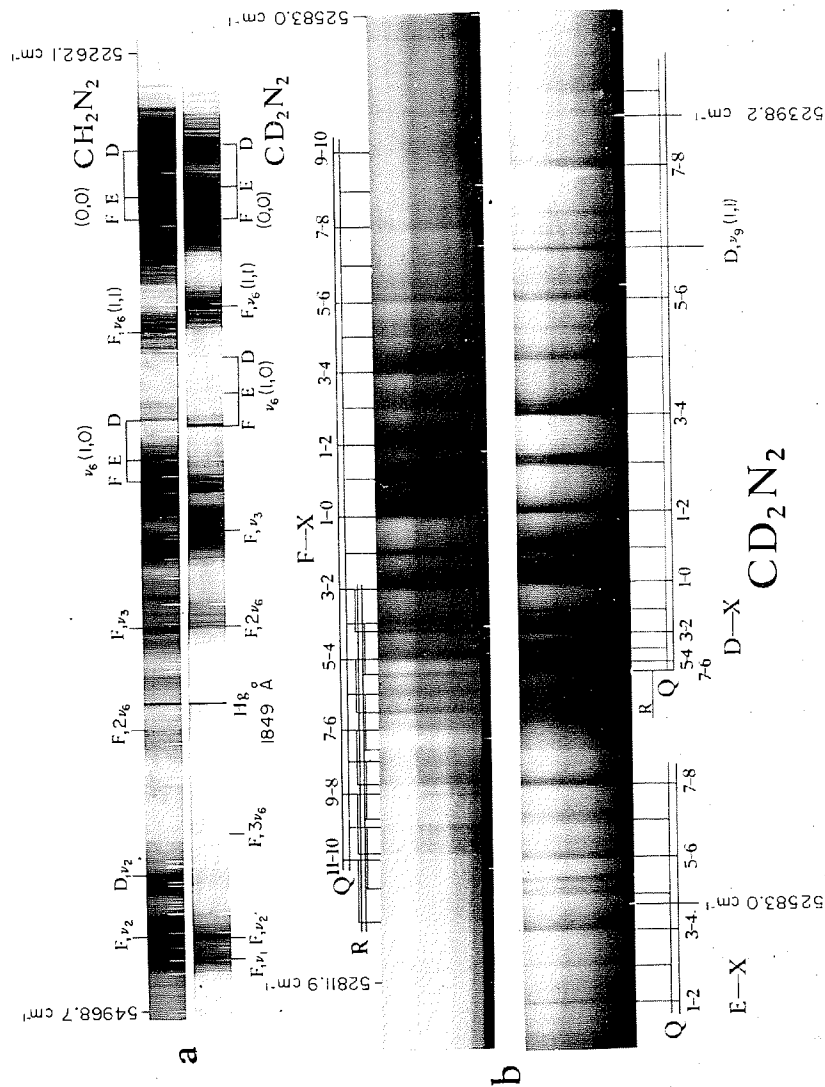


FIG. 1. (a) The region 1950–1820 Å in the spectra of  $\text{CH}_3\text{N}_2$  and  $\text{CD}_3\text{N}_2$  at room temperature; absorption length one meter, pressure of gas about 0.1 mm Hg. (b) The three (0, 0) bands of the 1900-Å system in the spectrum of  $\text{CD}_3\text{N}_2$  at  $-77^\circ\text{C}$ ; above,  $F-X$  (0, 0); below,  $E-X$  (0, 0) and  $D-X$  (0, 0). The  $K$  numbering of the  $Q$  branches and  $\mu R$  heads is indicated.

PLATE II

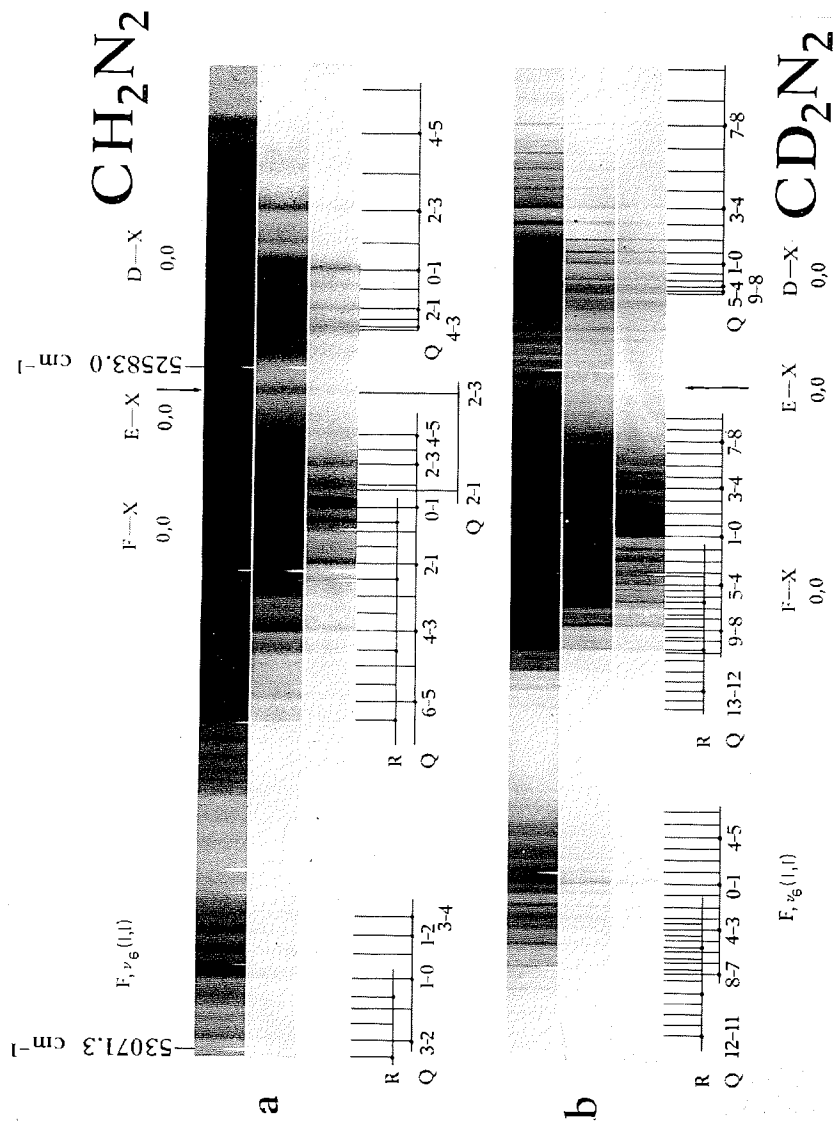


Fig. 2. Room-temperature spectra of (a)  $\text{CH}_2\text{N}_2$  and (b)  $\text{CD}_2\text{N}_2$  in the region 1885–1910 Å showing the D, E, F-X (0, 0) bands and the F-X,  $\nu_6(1, 1)$  band. The K numbering of the Q branches and R heads is indicated; absorption length 1 meter, gas pressures 0.1 mm, 0.03 mm, 0.01 mm Hg, approximately.

The  $K$  structure of the  $F-X$  (0, 0) band of  $\text{CD}_2\text{N}_2$  was analyzed using values of  $\Delta_2 F''(K)$  from the  $D-X$  (0, 0) band, together with the intensity alternation and the positions of the first lines of the unresolved  $^P P$  branches. Again the band was found to be a Type C band, since calculations of trial spectra showed that the  $^R Q$  branch of the 1-0 subband would have been degraded to shorter wavelengths had the band been Type B.

The apparent values of  $A' - \bar{B}'$ , neglecting  $D_K$  terms, are given in Table II. From the ultraviolet spectrum  $A'' - \bar{B}''$  for  $\text{CD}_2\text{N}_2$  is found to be  $4.239 \text{ cm}^{-1}$ , as compared to the infrared value of  $4.253 \pm 0.010 \text{ cm}^{-1}$ . Table III gives the positions of the assigned subband heads.

When the  $Q$  branches of the subbands in the  $F-X$  (0, 0) band of  $\text{CD}_2\text{N}_2$  had been identified, many features still remained unexplained. Their identities followed from comparison of the plates taken at different temperatures. As can be seen from comparison of Fig. 1(b), taken at  $-77^\circ \text{C}$ , with Fig. 2(b), taken at room temperature, the  $Q$  heads are stronger at the lower temperature, while the leading edges of the diffuse extra features are much more intense and head-like at room temperature. This indicated that the extra features are  $^R R$  heads, corresponding to the  $^R Q$  heads some  $12 \text{ cm}^{-1}$  to the red, since the  $R$  heads are calculated to occur at about  $J = 40$ , which would be appreciably more populated at room temperature than at  $-77^\circ \text{C}$ . Only one feature is then left unexplained, and this lies within  $2 \text{ cm}^{-1}$  of the predicted position of the most intense subband of the unobserved  $D-X$ ,  $\nu_6$  (1, 1) band. The apparent narrow gaps in the structure are the spaces between the first lines of the  $^R R$  branches of given subbands, and the  $^R R$  heads of adjacent subbands.

The value of  $\bar{B}$  for the  $v = 0$  level of the  $F^1 B_1$  state was obtained from the formula

$$-4\Delta\nu_{R0}(\bar{B}' - \bar{B}'') = (\bar{B}' + \bar{B}'')^2$$

(in which  $\Delta\nu_{R0}$  is the distance of the  $R$  head from the subband origin), assuming the value  $\bar{B}'' = 0.3234 \text{ cm}^{-1}$  given by Sheridan (1962). The position of the first line of the  $^R R$  branch can also be found (by substituting  $J = K''$  in the usual formula), and the  $J$  number at the  $^R R$  head is

$$J_{R \text{ head}} = (\bar{B}'' - 3\bar{B}')/2(\bar{B}' - \bar{B}'').$$

TABLE II  
Rotational constants (in  $\text{cm}^{-1}$ ) for the (0, 0) bands\*

		$\nu_0$	$A - \bar{B}$	$\bar{B}$	
$\text{CH}_2\text{N}_2$	$F^1 B_1$	52688.7	9.98†	0.359	
	$E(^1 B_2)$	52649	—	—	
	$D^1 B_1$	52520.9	6.80†	0.36 <sub>2</sub>	
	$X^1 A_1$	0	8.743	0.3694	
$\text{CD}_2\text{N}_2$	$F^1 B_1$	52697.06	4.213†	$\sim 0.315$	$\zeta_{FE} = 0.45_7$
	$E(^1 B_2)$	52618.1	4.21†	0.3182	
	$D^1 B_1$	52502.90	3.599†	0.3183	$\zeta_{DE} = 0.78_9$
	$X^1 A_1$	0	4.239	0.3234	

\*The  $\bar{B}$  values for the  $X^1 A_1$  states are taken from Sheridan (1962) and the  $A'' - \bar{B}''$  for  $\text{CH}_2\text{N}_2$  is taken from Moore (1963).

†Apparent values.

TABLE III  
Subband heads of the perpendicular bands ( $Q$  branches)

Band	CH <sub>2</sub> N <sub>2</sub>				CD <sub>2</sub> N <sub>2</sub>			
	$K$	cm <sup>-1</sup>	$K$	cm <sup>-1</sup>	$K$	cm <sup>-1</sup>	$K$	cm <sup>-1</sup>
$D-X$ (0, 0)	1-0	52527.5			1-0	52506.72		
	2-1	52540.3	0-1	52512.2	2-1	52513.75	0-1	52499.23
	3-2	52548	1-2	52493.2	3-2	52518.42	1-2	52490.27
	4-3	52554.8	2-3	52469.5	4-3		2-3	52478.93
			3-4	52441.7	5-4	52525.51	3-4	52467.46
			4-5	52415.3	6-5		4-5	52454.82
			5-6	52382.9	7-6	52527.42	5-6	52440.84
			6-7	52350.2	8-7		6-7	52426.41
			7-8		9-8	52522.14	7-8	52408.83
			8-9	52276.4			8-9	52390.5
							9-10	52370.10
$F-X$ (0, 0)	1-0	52698.5			1-0	52701.48		
	2-1	52721.2	0-1	52679.9	2-1	52709.61	0-1	52693.02
	3-2	52744.3	1-2	52664.4	3-2	52717.95	1-2	52684.44
	4-3	52768.3	2-3	52650.9	4-3	52726.47	2-3	52675.55
	5-4	52793.4	3-4	52641.2	5-4	52734.81	3-4	52667.25
	6-5	(52816.5)	4-5	52629.3	6-5	52742.77	4-5	52658.48
	7-6	(52848.3)			7-6	52751.57	5-6	52650.39
					8-7	52760.22	6-7	52641.05
					9-8	52767.08	7-8	52632.89
					10-9	52776.42	8-9	52624.47
					11-10	52782.66	9-10	52614.92
$E-X$ (0, 0)							1-2	52605.39
	2-1	52668.6	2-3	52598.7			2-3	52596.92
							3-4	52588.84
							4-5	52580.16
							5-6	52571.81
							6-7	52563.76
							7-8	52554.60
$F-X, \nu_6$ (1, 1)	1-0	53015.7			1-0	52955.46		
	2-1	53039.0	0-1	52999.20	2-1	52965.45	0-1	52948.65
	3-2	53062.6	1-2	52985.9	3-2	52973.39	1-2	52940.40
					4-3	52981.08	2-3	52931.86
			3-4	52974.2	5-4	52990.09	3-4	52923.02
					6-5	52997.06	4-5	52915.34
					7-6	53005.63	5-6	52905.2
					8-7	53012.66	6-7	52897
							7-8	52891.59
					10-9	53030.68	8-9	52884.05

For example, in the 11-10 subband, the separation of the  $^R R$  and  $^R Q$  heads is 13.5 cm<sup>-1</sup>, which (allowing for the missing lines in the  $Q$  branch, by using a successive approximation method) gives  $\bar{B}' = 0.3153$  cm<sup>-1</sup>,  $J_{R \text{ head}} = 38$ , and  $\nu_{R \text{ head}} - R(10) = 6.56$  cm<sup>-1</sup>. This last quantity is observed, in the spectrum, to be 6.1 cm<sup>-1</sup>.

For CH<sub>2</sub>N<sub>2</sub>, analysis of the  $K$  structures of the  $D-X$  (0, 0) and  $F-X$  (0, 0) bands proceeded on similar lines. The  $Q$ -branch heads are very diffuse, but the subbands were numbered without difficulty using Moore's (1963) infrared data, together with the intensity alternation. The  $F-X$  (0, 0) band of CH<sub>2</sub>N<sub>2</sub> was found to be strongly "violet"-degraded, in contrast to the same band of CD<sub>2</sub>N<sub>2</sub>, which is undegraded.

The  $K$  structure of the  $F-X$  (0, 0) band of  $\text{CH}_2\text{N}_2$  becomes complicated after the 6-5 subband, and extra heads, besides the  $^R R$  heads, appear (see Fig. 2(a)). These heads are in approximately the positions expected for the intense subband heads of the  $D-X$ ,  $\nu_6$  (1, 1) band, and there is little doubt that the  $52848.3\text{ cm}^{-1}$  feature corresponds to the 1-0  $^R Q$  head of this band. No unambiguous  $K$  structure analysis was possible for this region owing to the diffuseness of the structure.

The separations of the  $^R R$  and  $^R Q$  heads in the  $F-X$  (0, 0) band of  $\text{CH}_2\text{N}_2$  give  $\tilde{B}' - \tilde{B}'' = -0.010\text{ cm}^{-1}$ . As in the  $\text{CD}_2\text{N}_2$  spectrum, no distinct  $^R R$  heads are observed for the  $D-X$  (0, 0) band: the heads are expected to be formed at about  $J = 60$ , at which the line intensity would be minimal.

The perpendicular-type  $F-X$ ,  $\nu_6$  (1, 1) bands, which lie immediately to the short-wavelength side of the (0, 0) group, in both  $\text{CH}_2\text{N}_2$  and  $\text{CD}_2\text{N}_2$ , also have well-resolved  $K$  structures, and could be analyzed. It was these bands that provided the key to the understanding of the parallel-type bands, since the most intense of the parallel-type bands lie to the short-wavelength side of these bands, by an amount nearly equal to  $\nu_6''$ , both for  $\text{CH}_2\text{N}_2$  and  $\text{CD}_2\text{N}_2$ .

Analysis of the  $F-X$ ,  $\nu_6$  (1, 1) bands was straightforward, since the  $K$  structures of the infrared bands corresponding to  $\nu_6$  have been analyzed, for  $\text{CH}_2\text{N}_2$  by Moore (1963), and for  $\text{CD}_2\text{N}_2$  by Moore and Pimentel (1964). The ground-state combination differences, where they can be observed in the ultraviolet spectrum, agree closely with those observed in the infrared, both for  $\text{CH}_2\text{N}_2$  and for  $\text{CD}_2\text{N}_2$ . Since the bands arise from the vibrational level  $\nu_6 = 1$ , which has  $B_1$  vibronic species, the intensity alternations are opposite to those of the (0, 0) bands, as can be seen in Fig. 2: for example, in the  $\text{CD}_2\text{N}_2$  spectrum, the linelike  $^R Q$  head of the 2-1 subband is "weak" in the  $F-X$  (0, 0) band, but "strong" in the  $F-X$ ,  $\nu_6$  (1, 1) band.

#### *B. Rotational Analysis of the $E-X$ (0, 0) Bands*

Analysis of the fragments of band between the (0, 0) bands of the  $D-X$  and  $F-X$  systems revealed the third electronic state of the trio,  $E(^1B_2)$ . Although the band type of the (0, 0) band cannot be determined, since the 1-0 and 0-1 subbands are not seen, it is possible to account satisfactorily for the apparent Coriolis interaction of the two  $^1B_1$  states if the  $E$  state is assumed to be  $^1B_2$ .

The evidence for this apparent interaction lies in the rotational constants  $A'$  for the two  $^1B_1$  states. If everything is normal, these should be in the ratio 2:1 for the two isotopic species, assuming the molecule to be planar in the upper states. Even if the two states are interacting directly, the mean of the two  $A'$  values should still be in the ratio 2:1. However, neither of these conditions is fulfilled, as can be seen from Table IV. Since the ratio is less than 2.0 for the  $D$  state, and greater than 2.0 for the  $F$  state, the observed  $K$  structures are compatible with the assumption of a third electronic state of species  $^1B_2$  lying between the two  $^1B_1$  states, which seems to be the  $E$  state.

All that can be seen of the  $E-X$  (0, 0) bands is a fragment of a band between the (0, 0) bands of the  $D-X$  and  $F-X$  systems, in  $\text{CD}_2\text{N}_2$ , and a single subband in the same place in  $\text{CH}_2\text{N}_2$ , together with another among the subbands of the



TABLE IV

	$A$ (cm <sup>-1</sup> )		Ratio
	CH <sub>2</sub> N <sub>2</sub>	CD <sub>2</sub> N <sub>2</sub>	
$X^1A_1$	9.112	4.562	1.997
$D^1B_1$	7.16	3.917	1.83
$F^1B_1$	10.34	4.538	2.28
$\frac{1}{2}(D + F)$	8.75	4.227	2.07

$F-X$  band. On the room-temperature plates of CD<sub>2</sub>N<sub>2</sub>, the region of the  $E-X$  band is very confused, but cooling the gas removes much overlying "hot" structure, and leaves the outline of the band clearly visible.

As can be seen in Fig. 1(b), the  $J$  structure of some of the subbands of the  $E-X$  (0, 0) band in CD<sub>2</sub>N<sub>2</sub> is sufficiently well resolved to enable an analysis to be made. The  $^3P$  branch of the 5-6 subband could be assigned (see Table I), and since its first line is  $P(6)$ , the numbering of the subbands could be established. The observed part was found to consist of the  $\Delta K = -1$  subbands from 1-2 to 7-8, in a band with a vibronic  $A$  lower state (from the intensity alternation). This lower state must be the ground state of the molecule, since the band is not sensitive to temperature change, and since the only two low-lying totally symmetric vibrational levels,  $2\nu_6''$  and  $2\nu_9''$ , can be eliminated as possibilities:  $2\nu_6''$  because the known values of  $\nu_6'$  and  $\nu_6''$  make it impossible for a band arising from  $2\nu_6''$  to appear in this place, and  $2\nu_9''$  because no band arising from  $\nu_9''$  itself, such as the 1-1 band, appears in the required position.

The intensity distributions of the  $E-X$  (0, 0) bands are peculiar. In CD<sub>2</sub>N<sub>2</sub>, the 1-2 subband is very weak compared to the 3-4 and 5-6 subbands, although it should have been much more intense, and the 1-0 and 0-1 subbands are missing altogether: at -77° C the latter are expected to fall in a clear region of the spectrum near the 9-10 subband of the  $F-X$  (0, 0) band. This behavior might be expected from a state which has no intensity of its own in absorption, but obtains its intensity from a nearby state that appears strongly in absorption, as a result of mixing induced by rotation about the  $z$  axis. In this case the 0-1 subband would be missing, and the 1-0 and 1-2 subbands would be weak. The reason for the appearance of the 1-2 subband seems to be the concentration of half the  $Q$ -branch intensity into a space of 0.5 cm<sup>-1</sup>. The 1-0 subband, which is calculated to have a much more strongly degraded  $Q$  branch, but the same total intensity, is absent. In the  $E-X$  (0, 0) band of CH<sub>2</sub>N<sub>2</sub> the only two subbands observed are 2-1 and 2-3, and no feature corresponding to the 0-1 subband has been seen, although this should be the most intense feature of the whole band if the intensity distribution were normal.

Besides the irregular intensity distribution of the  $E-X$  (0, 0) bands, further evidence that state  $E$  is responsible for the observed perturbation of the  $K$  structures of states  $D$  and  $F$  comes from the fact that the position of state  $E$  relative to  $D$  and  $F$  in CH<sub>2</sub>N<sub>2</sub> can be predicted, using only the observed  $K$  structures of states  $D$  and  $F$ , and the interaction constants derived from the CD<sub>2</sub>N<sub>2</sub> spectrum.

The problem is essentially similar to the coupling of  $\nu_5''$ ,  $\nu_6''$ , and  $\nu_9''$  described by Moore, and the interaction matrix may be written

$$\begin{bmatrix} V_1 & -2AK\zeta_{FE} & 0 \\ -2AK\zeta_{FE} & -V_1 + V_2 & -2AK\zeta_{DE} \\ 0 & -2AK\zeta_{DE} & -V_2 \end{bmatrix},$$

where  $V_1$  and  $V_2$  are the energies of states  $F$  and  $D$  referred to the mean energy of the three states, and  $\zeta_{FE}$  and  $\zeta_{DE}$  refer to the interactions  $F:E$  and  $E:D$  respectively. Provided that the terms  $2AK\zeta$  are small compared to the energy differences between the states, the energy levels can be approximated by

$$W_F = \nu_0 + V_1 + (A - \bar{B})K^2 + 4A^2K^2\zeta_{FE}^2/(2V_1 - V_2),$$

$$W_E = \nu_0 - V_1 + V_2 + (A - \bar{B})K^2 + 4A^2K^2[\zeta_{DE}^2/(2V_2 - V_1) + \zeta_{FE}^2/(V_2 - 2V_1)],$$

$$W_D = \nu_0 - V_2 + (A - \bar{B})K^2 + 4A^2K^2\zeta_{DE}^2/(V_1 - 2V_2).$$

The average term value of the three states observed in  $\text{CD}_2\text{N}_2$  is

$$W = \nu_0 + (A - \bar{B})K^2,$$

which, when plotted against  $K^2$ , gives  $\nu_0 = 52606.0_6 \text{ cm}^{-1}$ , and  $A - \bar{B} = 4.026 \text{ cm}^{-1}$ . Then, plotting  $W_F - W$  and  $W_D - W$  against  $K^2$  gives  $|\zeta_{FE}| = 0.45_7$ ,  $|\zeta_{DE}| = 0.78_9$ ,  $2V_1 - V_2 = 78.5 \text{ cm}^{-1}$ , and  $V_1 - 2V_2 = -114.0 \text{ cm}^{-1}$ . These constants reproduce the observed term values of  $\text{CD}_2\text{N}_2$  very well, though evaluation of the matrix shows that the true  $\zeta_{DE}$  is very slightly greater than that given by the approximate formulae.

For  $\text{CH}_2\text{N}_2$ , using only the "apparent"  $A'$  values of the  $D-X$  (0, 0) and  $F-X$  (0, 0) bands (taken from the levels with  $K \leq 3$ ), a value of the "true"  $A'$  double that found for  $\text{CD}_2\text{N}_2$ , and  $\zeta$ 's carried over from the  $\text{CD}_2\text{N}_2$  spectrum, the quantity  $2V_1 - V_2$  for  $\text{CH}_2\text{N}_2$  is calculated to be  $37.8 \pm 2 \text{ cm}^{-1}$ , and the separation of the  $D$  and  $F$  states,  $V_1 + V_2$ , is calculated to be  $162.6 \pm 10 \text{ cm}^{-1}$ . This separation, as observed in the spectrum, is  $167.8 \text{ cm}^{-1}$ , satisfactorily within the limits imposed by the probable error in the "apparent" rotational constants. The quantity  $2V_1 - V_2$  cannot be checked directly, but substituting the calculated values of  $V_1$  and  $V_2$  in the matrix, the term values of the  $v = 0$  level of state  $E$  in  $\text{CH}_2\text{N}_2$  can be worked out, and the unassigned subband between the  $D-X$  (0, 0) and  $F-X$  (0, 0) bands is found to lie within  $5 \text{ cm}^{-1}$  of the position predicted for the 2-3 subband of the  $E-X$  (0, 0) band. Since the other feature attributable to the  $E-X$  system is separated from it by the ground-state interval  $\Delta_2 F''$  ( $K = 2$ ), it was possible to assign these two features as the  $Q$  branches of the 2-1 and 2-3 subbands of the  $E-X$  (0, 0) band. These subbands are the only two expected to have even moderate intensity in  $\text{CH}_2\text{N}_2$ , assuming the intensity to be borrowed by Coriolis coupling.

### C. Vibrational Analysis

The vibrational bands of the  $1900 \text{ \AA}$  system can be divided conveniently into those making up progressions in  $\nu_6$  (which include all the narrow parallel-type bands), and those involving the totally symmetric fundamentals.

The assignments of the  $\nu_6$  progressions follow from the rotational analyses of the  $F-X$ ,  $\nu_6$  (1, 1) bands, and the realization that the interval between them and the most intense of the vibrationally forbidden parallel-type bands,  $F-X$ ,  $\nu_6$  (1, 0), in both  $\text{CH}_2\text{N}_2$  and  $\text{CD}_2\text{N}_2$ , is the ground-state frequency  $\nu_6''$ . Confirmation of the assignment comes from observation, on one set of plates, of the bands  $F-X$ ,  $\nu_6$  (1, 0) and  $\nu_6$  (1, 1) of  $\text{CHDN}_2$ , separated by an interval nearly equal to Moore and Pimentel's (1964) infrared value of  $\nu_6$  for  $\text{CHDN}_2$ .

The ground-state combination differences  $\Delta_2 F''(K)$  found in the  $F-X$ ,  $\nu_6$  (1, 1) band of  $\text{CH}_2\text{N}_2$  are specific for  $\nu_6''$ , since Moore has shown that the level  $v_6 = 1$  of the ground state is strongly coupled to the level  $v_3 = 1$  by Coriolis coupling, and that the energy levels are perturbed. Thus, observation of this same series of perturbed energy levels in the ultraviolet spectrum makes the assignment fairly certain.

Members of the progressions in  $\nu_6$  for all three electronic states can be identified, and the three vibrational frequencies  $\nu_6'$  are found to be quite similar (by some coincidence), though appreciably different from the ground-state frequency  $\nu_6''$ . As a result of this, the pattern formed by the  $\nu_6$  (1, 0) bands of the three transitions is very like that formed by the (0, 0) bands. The  $\nu_6$  (1, 0) bands of the  $E-X$  system are a good example of Coriolis coupling causing  $A_2 - A_1$  vibronic bands to appear in absorption. The  $E-X$ ,  $\nu_6$  (1, 0) band is much more intense in  $\text{CH}_2\text{N}_2$  than in  $\text{CD}_2\text{N}_2$ , since its intensity is borrowed from the  $F-X$ ,  $\nu_6$  (1, 0) band: the amount of intensity borrowed must be proportional to  $K^2 A^2 / \Delta E$  for Coriolis coupling, and, not only is the separation  $\Delta E$  smaller in  $\text{CH}_2\text{N}_2$  than in  $\text{CD}_2\text{N}_2$ , but the  $A'$  value for  $\text{CH}_2\text{N}_2$  is twice that for  $\text{CD}_2\text{N}_2$ .

By arguments similar to those used for the  $F-X$ ,  $\nu_6$  (1, 0) and  $\nu_6$  (1, 1) bands, many other bands can be assigned to these  $\nu_6$  progressions. All the assigned bands to the long-wavelength side of the (0, 0) group arise from  $\nu_6''$  or  $2\nu_6''$  in the transitions  $D-X$  and  $F-X$ ;  $2\nu_6''$  for  $\text{CD}_2\text{N}_2$  is found to be  $666 \text{ cm}^{-1}$ , in close agreement with Moore and Pimentel's value, but, unless the subband intensities in the  $F-X$ ,  $\nu_6$  (0, 2) band are somehow unusual, the value of  $2\nu_6''$  for  $\text{CH}_2\text{N}_2$  disagrees with Moore's value by  $20 \text{ cm}^{-1}$ . To the short-wavelength side of the (0, 0) group the bands  $F-X$ ,  $\nu_6$  (2, 0) are readily identified for  $\text{CH}_2\text{N}_2$ ,  $\text{CHDN}_2$ , and  $\text{CD}_2\text{N}_2$ , while  $F-X$ ,  $\nu_6$  (3, 0) and (3, 1) can be seen in the  $\text{CD}_2\text{N}_2$  spectrum. The bands involving odd values of  $\Delta v_6$  are Type A, and those involving even values are Type C. The anharmonicity of  $\nu_6$  in the  $F$  state, as in the ground state, is positive, which is often the case for an out-of-plane bending vibration. A Deslandres table for  $\nu_6$  in the  $F-X$  transition is given in Table V.

It seems that the molecule remains planar in the upper states (despite the appearance of progressions in the  $\text{CH}_2$  out-of-plane bending vibration,  $\nu_6$ ), since successive members of the progressions have alternating band types, and since the results of the rotational analysis are not inconsistent with a planar upper state.

The band envelopes of the vibrationally forbidden parallel-type bands are peculiar. Since perpendicular bands involving the upper and lower levels of the

TABLE V  
Deslandres table for the vibration  $\nu_6$  in the  $F-X$  system\*  
(Estimated band origins, in  $\text{cm}^{-1}$ )

	$\nu'' \backslash \nu'$	0		1		2		3	
CH <sub>2</sub> N <sub>2</sub>	0	52688.6 <i>C</i>	726.3	53414.9 <i>A</i>	741.1	54156.0 <i>C</i>			
		404.3		407.1		399.4			
	1	52284.3 <i>A</i>	723.5	53007.8 <i>C</i>	748.8	53756.6 <i>A</i>			
		465.8							
	2	(51818.5) <i>C</i>							
CD <sub>2</sub> N <sub>2</sub>	0	52695.8 <i>C</i>	574.3	53270.1 <i>A</i>	580.8	53850.9 <i>C</i>	585.0	54435.9 <i>A</i>	
		317.6		318.8		318.5		317.6	
	1	52378.2 <i>A</i>	573.1	52951.3 <i>C</i>	581.1	53532.4 <i>A</i>	585.9	54118.3 <i>C</i>	
		348.9							
	2	52029.3 <i>C</i>							

\**C* and *A* refer to the band types.

parallel-type  $F-X$ ,  $\nu_6$  (1, 0) and  $D-X$ ,  $\nu_6$  (0, 1) bands have been analyzed, the lines of the branches in these parallel-type bands can be calculated. They are found to fall in the expected positions, but with unusual intensities: the *R* branches are found to be far stronger than expected. No explanation for this anomaly is offered.

The totally symmetric vibration frequencies of the  $F$  state presented no problems, for  $\nu_1'$  and  $\nu_2'$  are similar to the ground-state frequencies, and  $\nu_3'$  and  $\nu_4'$  could be assigned with the aid of the Redlich-Teller isotope rule. The totally symmetric vibrations of the  $F$  state, with their frequencies (in  $\text{cm}^{-1}$ ), are:

	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$
$\text{CH}_2\text{N}_2$	2908.8	2069.7	1174.1	792.0
$\text{CD}_2\text{N}_2$	2150.8	2048.7	874.9	734.3

Almost all the remaining bands could be assigned in terms of the totally symmetric vibrations, with or without  $\nu_6$ , of the  $D$  and  $F$  electronic states (see Table VI). The only intense doubtful feature is the diffuse band at  $53621 \text{ cm}^{-1}$  in the spectrum of  $\text{CH}_2\text{N}_2$ , which is tentatively assigned as  $D-X$ ,  $\nu_3$  (1, 0).

#### 4. ELECTRONIC TRANSITIONS AT SHORTER WAVELENGTHS

Most of the intense transitions lying in the region between  $1780 \text{ \AA}$  and  $1350 \text{ \AA}$  can be assigned to a single Rydberg series, beginning with the bands at  $1670 \text{ \AA}$ , and leading to a limit at  $1378 \text{ \AA}$ . This series can be described by the formula

$$\nu = 72585 - 109737.3/(n - 0.10)^2 \text{ cm}^{-1},$$

which gives the first I.P. of diazomethane as  $8.999 \pm 0.001 \text{ ev}$ . A reproduction of the higher members of this series in  $\text{CH}_2\text{N}_2$  has been given by Herzberg (1961).

TABLE VI  
Vibrational bands of the 1900 Å system  
(Measurements of the most intense feature of each band are given.  
Where known, the  $K$  assignment is also given.)

cm <sup>-1</sup>	CH <sub>2</sub> N <sub>2</sub>	cm <sup>-1</sup>	CD <sub>2</sub> N <sub>2</sub>
51809.8	$F-X, \nu_6(0, 2)$	51715.8	? $D-X, \nu_9(0, 2)$
52125.3	$D-X, \nu_6(0, 1)$	51831.9	$D-X, \nu_6(0, 2), 0-1$
52295.3	$F-X, \nu_6(0, 1)$	51949.9	? $F-X, \nu_9(0, 2)$
52512.2	$D-X, (0, 0), 0-1$	52026.9	$F-X, \nu_6(0, 2), 0-1$
52598.7	$E-X, (0, 0), 2-3$	52199.4	$D-X, \nu_6(0, 1)$
52680.9	$F-X, (0, 0), 0-1$	52397.2	$F-X, \nu_6(0, 1)$
52848.3	$D-X, \nu_6(1, 1), 1-0$	52506.7	$D-X, (0, 0), 1-0$
53015.7	$F-X, \nu_6(1, 1), 1-0$	52618.1	$E-X, (0, 0), \nu_0$ (calc)
53266.0	$D-X, \nu_6(1, 0)$	52700.0	$F-X, (0, 0), 1-0$
53372.6	$E-X, \nu_6(1, 0)$	52752.9	$D-X, \nu_6(1, 1), 0-1$
53427.9	$F-X, \nu_6(1, 0)$	52948.7	$F-X, \nu_6(1, 1), 0-1$
53472.9	$F-X, \nu_4(1, 0)$	53039.4	$D-X, \nu_6(1, 0)$
53620.6	? $D-X, \nu_3(1, 0)$	53188.5	$E-X, \nu_6(1, 0)$
53769.6	$F-X, \nu_6(2, 1)$	53282.1	$F-X, \nu_6(1, 0)$
53855.0	$F-X, \nu_3(1, 0), 0-1$	53366.1	$F-X, \nu_3(1, 0)$
53995.1	? $D-X, \nu_6(2, 0)$	53434.3	$F-X, \nu_6(2, 1)$
54147.3	$F-X, \nu_6(2, 0), 0-1$	53542.4	$F-X, \nu_3(1, 0)$
54305.6	?	53846.3	$F-X, \nu_6(2, 0), 0-1$
54528.7	?	54000.8	?
54569.4	$D-X, \nu_2(1, 0)$	54113.8	$F-X, \nu_6(3, 1)$
54750.6	$F-X, \nu_2(1, 0)$	54341.5	?
54920.9	?	54441.9	$F-X, \nu_6(3, 0)$
55025.5	{ $F-X, \nu_3(2, 0)$ $F-X, \nu_2(1, 0), \nu_6(1, 1)$	54593.0	? $D-X, \nu_2(1, 0)$
55507.8	$F-X, \nu_2(1, 0), \nu_6(1, 0)$	54748.7	$F-X, \nu_2(1, 0)$
55589.7	$F-X, \nu_1(1, 0)$	54850.8	$F-X, \nu_1(1, 0)$
55917.3	$F-X, \nu_2(1, 0), \nu_3(1, 0)$	55015.9	$F-X, \nu_2(1, 0), \nu_6(1, 1)$
56239.7	$F-X, \nu_2(1, 0), \nu_6(2, 0)$	55352.6	? $F-X, \nu_2(1, 0), \nu_6(1, 0)$
		55413.2	$F-X, \nu_1(1, 0), \nu_6(1, 0)$
		55526.5	$F-X, \nu_2(1, 0), \nu_3(1, 0)$
		55625.5	$F-X, \nu_1(1, 0), \nu_3(1, 0)$

The observed quantum defect, 0.10 (or 1.10), is consistent with a  $d$  or an  $s$  Rydberg series, when only first-row elements are present. Since there are several intense heads for each member of the series, it is presumably an  $nd$  Rydberg series.

A perpendicular-type band system resembling the 1900 Å  $F-X$  system in certain respects appears at 1585 Å. If these two systems are assumed to form the first two members of a Rydberg series, a quantum defect of 0.67 (characteristic of a  $p$  Rydberg series) and an I.P. of 9.06 eV are calculated; the closeness of this limit to that found from the  $d$  series (where many more members are found, and the extrapolation to the limit is shorter) seems to support the Rydberg assignment. No further members of this series can be found.

Weaker parallel-type bands are seen, both in this  $4p$  system, and in the nearby  $3d$  system at 1670 Å. In the 1585 Å system ( $4p$ ), the strongest of these parallel-type bands appears 343 cm<sup>-1</sup> to the long-wavelength side of the (0, 0) band, and shows only a small isotope shift; since this frequency is not one of the ground-state frequencies of the molecule, the band seems to be the (0, 0) band of another electronic transition, which can be assigned as the  $A_1$  component of the  $4p$  group. On this basis a few vibrational assignments can be made, but since the bands are all extremely diffuse, these assignments cannot be considered definitive.

In the  $d$  Rydberg series the vibrational structure is again completely diffuse, and except for the  $(0, 0)$  bands, extremely weak. The only vibration that can be definitely assigned is  $\nu_2'$ , which appears in nearly all the Rydberg transitions, with a frequency closely similar to the ground-state frequency. From the comparative absence of strong vibrational transitions it seems likely that the ground state of the ion is planar, and similar in dimensions to the ground state of the molecule.

An intense band system, which does not fit into any Rydberg series, occurs at  $1757 \text{ \AA}$ . Its structure is completely diffuse in both  $\text{CH}_2\text{N}_2$  and  $\text{CD}_2\text{N}_2$ , and no assignment can be made, either of the direction of the transition moment or of the vibrations appearing. This system is different from all the others in that the second strong band ( $57300 \text{ cm}^{-1}$ ) is considerably more intense than the first ( $56870 \text{ cm}^{-1}$ ), perhaps indicating a larger change of molecular dimensions than in any of the other transitions. However, vibrational repetitions of this pattern and the absence of further members of this  $430 \text{ cm}^{-1}$  progression suggest that more than one electronic state is present.

The positions of the prominent bands of the higher electronic states are given in Table VII.

Beyond  $1400 \text{ \AA}$ , where the  $d$  Rydberg series becomes faint, further extremely broad diffuse bands of very great intensity appear. They show only small isotope shifts, but their irregular spacings make it difficult to fit them into a Rydberg series converging to a higher limit.

## 5. DISCUSSION

By analogy with the configurations of  $\text{AB}_2$  molecules, the ground state of diazomethane can be written

$$KKK(1a_1)^2(1b_2)^2(2a_1)^2(3a_1)^2(2b_2)^2(1b_1)^2(3b_2)^2(2b_1)^2 \quad {}^1A_1.$$

The lowest-lying transitions, excluding triplets, will then be to  ${}^1A_2$  and  ${}^1A_1$  electronic states, by promotion of an electron from either the  $(2b_1)$  or  $(3b_2)$  orbital, whichever lies higher, to the  $(3b_1)$  and  $(4b_2)$  orbitals: the observed transitions in the visible and near ultraviolet might correspond to these.

Lying further in the ultraviolet will be the Rydberg transitions to the  $(3sa_1)$ ,  $(3pa_1)$ ,  $(3pb_1)$ , and  $(3pb_2)$  orbitals. However, as we have seen, absorption transitions to three states, two of species  $B_1$  and one of species  $B_2$ , occur near  $1900 \text{ \AA}$ , and it is difficult to see how they can all be Rydberg transitions. If the two  $B_1$  states are assumed to arise by promotion of an electron from a  $b_1$  orbital to the two Rydberg  $a_1$  orbitals, then the other states of the  $3p$  group are  $A_1$  and  $A_2$ , and no  $B_2$  state would be expected. Since the  $B_2$  state observed seems to have no intensity of its own in absorption, it is possible that it corresponds to a two-electron transition, but this suggestion is no more than tentative.

The presence of vibrationally forbidden bands in an electronic transition of diazomethane seems to be nothing exceptional, as other instances of spectra, in which the vibrational selection rules are broken, can be quoted (see, for example, Innes, Simmons, and Tilford's (1963) account of the  $3200 \text{ \AA}$  transition

TABLE VII  
Prominent bands of higher electronic transitions (in  $\text{cm}^{-1}$ )

	[1770 Å]	3d	4p	4d	5d	6d	7d
CH <sub>2</sub> N <sub>2</sub>	56896 0-0	59497.1 3d'	62831.4 4p' (  ) 0-0	65381.4 max	68004.3 max	69437.1	70276.4
	56970	59618.5 max 3d''	63178.7 4p'' (⊥) 0-0	65468.1 edge	68052.9	69476.1	70306.0
	57323*	59669.9 edge 3d'''	63472.5 4p' + ν <sub>6</sub>	65571.8	68142.3	69516*	
	58195	59833.6 max 3d''''	63736.5 (sharp)	65652.8	68174.3	69964	
	58677*	59851.0 edge	63810.2 4p'' + ν <sub>6</sub> (  )	66019	68868		
	59138*	60074*	64233	66376.3	69002.1 ν <sub>3</sub>		8d: 70824.5
		60210	64859	66626	69189		70840.6
		60477*		67471.1 ν <sub>2</sub>	[70094.4 ν <sub>2</sub> ]		9d: 71223.4
		60793 3d''' + ν <sub>4</sub> ?		67564			10d: 71467.4
		61057		67674			71486.7
		61227 3d''' + ν <sub>3</sub> ?		67752			
		61703 (sharp)					
		61933 3d''' + ν <sub>2</sub>					
CD <sub>2</sub> N <sub>2</sub>	56852 0-0	59577.6 3d'	62820.2 4p' (  ) 0-0	65354.3	67994.6 max	69422.5	70255.8
	56908	59620.1 3d''	63165.5 4p'' (⊥) 0-0	65452.4 max	68046.0	69442.7	70296.1
	57247	59719.6 3d'''	63397.7 4p'' + ν <sub>6</sub> (1, 1) ?	65591.1	68115.5	69642*	
	57603*	59731.1 3d''''	63710.1	65658.8	68167.0	69971	
	58243	59852.0 3d''''	64175.3	65861	68845		
	58750	60760 3d''' + ν <sub>4</sub> ?	64269.5	66007	68960.3		8d: 70816.3
		60881	64781	66349	69121.3		70842.6
		61106 3d''' + ν <sub>3</sub> ?	64940	66530	[70092.7 ν <sub>2</sub> ]		9d: 71193.1
		61310		67537.5 ν <sub>2</sub>			71202.1
		61745		67693			10d: 71456.8
		61927 3d''' + ν <sub>2</sub>		67734			71465.8

\*Denotes overlapped by ethylene band (C<sub>2</sub>H<sub>4</sub> or C<sub>2</sub>D<sub>4</sub>).

in pyrazine). In the 1900 Å band system of diazomethane the parallel-type bands involving odd quanta of a nontotally symmetric vibration, in a transition where the (0, 0) band is perpendicular-type, must be ascribed to vibronic mixing with an unidentified allowed transition.

#### ACKNOWLEDGMENTS

I would like to thank Dr. J. T. Hougen for his assistance with the theory of Coriolis interactions, and Dr. G. Herzberg and Dr. A. E. Douglas for their encouragement, and for suggesting improvements to the manuscript. I would also like to thank Mr. J. Shoosmith and Mr. F. Alberti, who took most of the plates.

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