

Infrared Spectra of CH₂N₂ and CD₂N₂

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From the 50-v monoisotopic spectra in Table II, the values of the abundance ratios $\text{CCl}_3^+/\text{CHCl}_3^+$ and $\text{CCl}_3^+/\text{CDCl}_3^+$ are 0.58₆ and 0.19₄, respectively. The ratio of these values, 3.0₂, is a measure of the relative probability of dissociating a hydrogen atom from CHCl_3 compared with CDCl_3 . Thus, for 50-v electrons the dissociation of a C—H bond is three times more frequent than the dissociation of a C—D bond. The data at 70 v confirm this result. This is comparable to the “ π -effect” reported for monodeuteromethane² which amounts to a factor of about 2.6.

The abundance ratios $\text{CCl}_2^+/\text{CHCl}_3^+$ and $\text{CCl}_2^+/\text{CDCl}_3^+$ at 50 v are 1.63 and 0.99, respectively. The ratio of these values, 1.65, is a measure of the relative probability of dissociating an H and a Cl atom compared with a D and a Cl atom. It is interesting to note the ratio of the relative abundances $\text{HCl}^+/\text{CHCl}_3^+$ (0.844) and $\text{DCl}^+/\text{CDCl}_3^+$ (0.524) gives a very similar value, 1.61. This suggests that the CCl_2^+ ion is formed primarily by the dissociation of HCl or DCl molecules rather than by dissociation into the separate atoms. If the former alternative were the only mechanism operative, the isotope effect would be very small. If, however, the

latter process were the only one, a factor of about three in the relative probabilities would be anticipated. The observed value of 1.6 suggests a process intermediate between these two limiting cases.

For the dissociation of a hydrogen atom and two chlorine atoms, the abundance ratios are equal within the estimated error. This is the result expected if an HCl or a DCl fragment and a chlorine atom were dissociated. There is some evidence for HCl_2^+ ions in the CHCl_3 spectrum. However, the abundance of these ions is very small and their origin is in doubt.

The probability of dissociating chlorine atoms is only slightly affected by the presence of an H or a D atom, since the abundance ratios $\text{CHCl}_2^+/\text{CHCl}_3^+$ and $\text{CDCl}_2^+/\text{CDCl}_3^+$ differ by only 4 percent. Furthermore, for the dissociation of two chlorine atoms the abundance ratios $\text{CHCl}^+/\text{CHCl}_3^+$ and $\text{CDCl}^+/\text{CDCl}_3^+$ are nearly identical.

The authors are grateful to Mr. W. M. Boyer and Mr. T. L. Brown for their assistance with the preparation of the deuteriochloroform and to Dr. Fred L. Mohler for his valuable suggestions concerning the interpretations of the mass spectra.

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Infrared Spectra of CH_2N_2 and CD_2N_2

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The infrared spectra of CH_2N_2 and CD_2N_2 have been investigated in the gas phase between 4500 and 400 cm^{-1} using a Perkin-Elmer spectrometer with LiF , NaCl , and KBr prisms.

The spectra have been correlated with a planar, nonlinear configuration for the diazomethane molecule with symmetry C_{2v} . The perpendicular type bands for both molecules are all overlapped or perturbed by neighboring absorption bands, so that no accurate values for the least moments of inertia have been obtained.

Two alternative schemes of assignments for the vibrational frequencies have been proposed and the thermodynamic functions for CH_2N_2 computed.

Potential-function calculations have been carried out.

INTRODUCTION

THE infrared spectrum of diazomethane is of interest, since it permits a complete assignment of the fundamental vibrational frequencies of the molecule and calculation of the thermodynamic properties. The physical properties of this molecule make it doubtful that these properties will ever be measured directly.

A preliminary investigation¹ has shown that the infra-

red spectrum is consistent with a planar, straight chain structure for the molecule, in agreement with the electron diffraction data.² The spectrum of the deuterated molecule has also been investigated and is in agreement with these conclusions. Complete assignments of vibration frequencies for the two molecules have been made and the potential function of the molecule calculated.

EXPERIMENTAL

Diazomethane was prepared by two different methods: (i) by the hydrolysis of nitrosomethylurea with NaOH , (ii) by the treatment of N -nitroso- β -methyl-

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¹ D. A. Ramsay, *J. Chem. Phys.* **17**, 666 (1949).

² H. Boersch, *Monatsh.* **65**, 311 (1935).

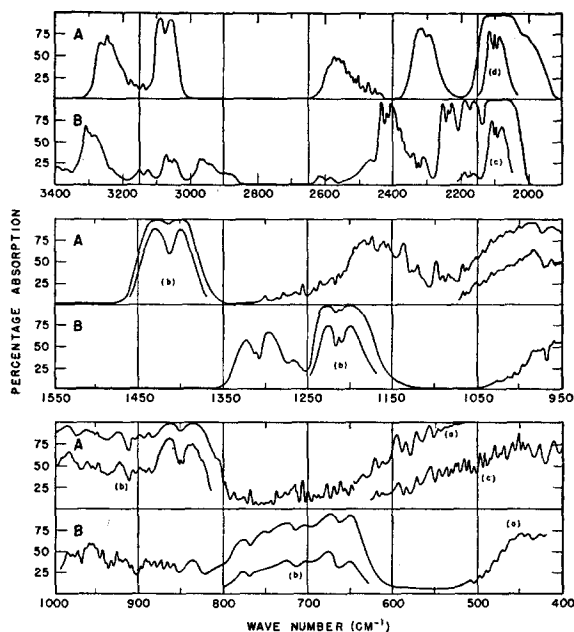


FIG. 1. Infrared spectra of (A) CH₂N₂, (B) CD₂N₂. Cell length=10 cm. Temperature=20°C. A. Pressure (a) 300-mm Hg, (b) 100-mm Hg, (c) 50-mm Hg, (d) 10-mm Hg. B. Pressure (a) 300-mm Hg, (b) 100-mm Hg, (c) 5-mm Hg.

aminoisobutylmethyl ketone with sodium dissolved in benzyl alcohol. Its spectrum was investigated independently in the two laboratories using Perkin-Elmer spectrometers with NaCl and KBr prisms. Glass absorption cells with KBr windows were used throughout, and vapor pressures of diazomethane from 5 to 650 mm Hg were investigated. The region above 2000 cm⁻¹ was also examined under higher resolving power using a Perkin-Elmer spectrometer with a LiF prism in the one case and a quartz spectrometer in the other. In all cases the agreement between the spectra obtained was extremely good. The appropriate absorption curves are reproduced in Fig. 1, and the frequencies of the absorption peaks are given in Tables I and III.

Deuterated diazomethane, CD₂N₂, was prepared by the hydrolysis of nitroso-methyl-*d*₃-urea³ with NaOD. Its vapor spectrum was investigated on a Perkin-Elmer spectrometer with NaCl, KBr, and LiF prisms (see Fig. 1 and Tables II and III). By comparison with the spectrum of CH₂N₂, it is seen that the amount of CH₂N₂ impurity in the CD₂N₂ is negligible. There is the possibility of CHDN₂ impurity, however.

Another attempt was made to prepare CD₂N₂ by decomposition of N-nitroso- β -methyl-*d*₃-aminoisobutylmethyl ketone with sodium dissolved in benzyl alcohol, but owing to an unexpected exchange with the solvent the deuterium in the intermediate was almost entirely lost in the last step of the preparation. The spectrum of this diazomethane sample, however, showed two ab-

TABLE I. Infrared frequencies and assignments for CH₂N₂.

cm ⁻¹	Int.	Band type	Assignment ^{b,c}
400-650 ^a	<i>s</i>	\perp	$\nu_9(b_2) = 487$ cm ⁻¹ (I) $\nu_7(b_1) = 586$ cm ⁻¹ (I) $\nu_9(b_2) = 456$ cm ⁻¹ (II) $\nu_7(b_1) = 487$ cm ⁻¹ (II)
650-825 ^a	<i>w</i>	\perp	$2\nu_7 - \nu_9 = 685$ (B ₂) (I) $\nu_6 - \nu_9 = 691$ (A ₂) ^d (II)
P 839 Q 852 R 864	<i>s</i>	\parallel	$\nu_4(a_1)$
P 900 Q — R 926	<i>m</i>	$\parallel?$	$2\nu_9(A_1)$ (II)
926	<i>m</i>	$\perp?$	$\nu_8 - \nu_9 = 928$ (B ₂) (I)
875-1050 ^a	<i>m</i>	\perp	$\nu_8(b_2) = 920$ cm ⁻¹
P 962 Q — R 986	<i>m</i>	\parallel	$2\nu_9(A_1)$ (I) $2\nu_7(A_1)$ (II)
1050-1325 ^a	<i>m</i>	\perp	$\nu_6(b_1) = 1147$ cm ⁻¹
P 1159 Q — R 1184	<i>m</i>	$\parallel?$	$2\nu_7(A_1)$ (I)
P 1401 Q — R 1429	<i>s</i>	\parallel	$\nu_8(a_1)$
2016	<i>w</i>	$?$	$\nu_4 + 2\nu_7 = 2024$ (A ₁) (I) $\nu_4 + \nu_6 = 1999$ (B ₁)
P 2087 Q 2101 R 2115	<i>vs</i>	\parallel	$\nu_2(a_1)$
P 2290 Q — R 2315	<i>m</i>	\parallel	$2\nu_6 = 2294$ (A ₁) $\nu_8 + 2\nu_9 = 2327$ (A ₁) (II)
2400-2650 ^a	<i>m</i>	\perp	$\nu_2 + \nu_9 = 2588$ (B ₂) (I) $\nu_2 + \nu_7 = 2588$ (B ₁) (II) $\nu_3 + \nu_6 = 2562$ (B ₁)
P 3062 Q — R 3088	<i>s</i>	\parallel	$\nu_1(a_1)$
Q 3140 Q 3158 Q 3175	<i>w</i>	\perp	$\nu_8(b_1) = 3150$ cm ⁻¹
P 3245 Q — R 3266	<i>m</i>	\parallel	$\nu_3 + 2\nu_8 = 3255$ (A ₁)
P 4168 Q — R 4193	<i>m</i>	\parallel	$2\nu_2(A_1)$
P 4275 Q — R 4300	<i>w</i>	\parallel	$\nu_5 + \nu_6 = 4297$ (A ₁)

^a The frequencies of the absorption peaks in this region are given in Table III.

^b I—Assignment I.

^c II—Assignment II.

^d Made active by Coriolis interaction.

³ Leitch, Gagnon, and Cambron, Can. J. Research 28, 256 (1950). The authors are indebted to Dr. Leitch for a sample of nitroso-methyl-*d*₃-urea.

TABLE II. Infrared frequencies and assignments for CD₂N₂.

cm ⁻¹	Int.	Band type	Assignment
<525 ^a	<i>s</i>	⊥	$\nu_9(b_2)=406\text{ cm}^{-1}$ (I) $\nu_7(b_1)=502\text{ cm}^{-1}$ (I) $\nu_9(b_2)=382\text{ cm}^{-1}$ (II) $\nu_7(b_1)=423\text{ cm}^{-1}$ (II)
<i>P</i> 650 <i>Q</i> — <i>R</i> 674	<i>s</i>		$\nu_4(a_1)$
701	<i>m</i>	?	$\nu_3-\nu_7=711$ (<i>B</i> ₁) (I)
724	<i>m</i>	?	$\nu_8+\nu_9-\nu_7=740$ (<i>B</i> ₁) (I)
<i>P</i> 753 <i>Q</i> — <i>R</i> 777	<i>m</i>		$\nu_4(a')$ (CHDN ₂)
800–1050 ^a	<i>m</i>	⊥	$\nu_8(b_2)=836\text{ cm}^{-1}$ $\nu_6(b_1)=960\text{ cm}^{-1}$
<i>P</i> 1200 <i>Q</i> 1213 <i>R</i> 1225	<i>s</i>		$\nu_3(a_1)$
1267	<i>w</i>	?	$\nu_2-2\nu_9=1284$ (<i>A</i> ₁) (I) $3\nu_7=1269$ (<i>B</i> ₁) (II)
<i>P</i> 1295 <i>Q</i> 1311 <i>R</i> 1323	<i>m</i>		$\nu_3(a')$ (CHDN ₂)
<i>P</i> 1846 <i>Q</i> — <i>R</i> 1869	<i>w</i>		$\nu_3+\nu_4=1875$ (<i>A</i> ₁)
<i>P</i> 2081 <i>Q</i> 2096 <i>R</i> 2107	<i>vs</i>		$\nu_2(a_1)$
<i>P</i> 2164 <i>Q</i> 2178 <i>R</i> 2188	<i>s</i>		$\nu_3+2\nu_7=2217$ (<i>A</i> ₁) (I) $2\nu_4+2\nu_7=2170$ (<i>A</i> ₁) (II)
<i>P</i> 2229 <i>Q</i> 2241 <i>R</i> 2253	<i>s</i>		$\nu_1(a_1)$
<i>P</i> 2318 <i>Q</i> 2329 <i>R</i> 2341	<i>w</i>		$\nu_8(a')$ (CHDN ₂) $\nu_4+2\nu_8=2334$ (<i>A</i> ₁)
<i>Q</i> 2363 <i>Q</i> 2373 <i>Q</i> 2382	<i>w</i>	⊥	$\nu_6(b_1)=2370\text{ cm}^{-1}$
<i>P</i> 2408 <i>Q</i> 2420 <i>R</i> 2432	<i>s</i>		$2\nu_3(A_1)$
2470	<i>w</i>	?	$\nu_6+\nu_7-\nu_9=2466$ (<i>B</i> ₂) (I) $\nu_2+\nu_9=2478$ (<i>B</i> ₂) (II)
<i>P</i> 2593 <i>Q</i> — <i>R</i> 2619	<i>w</i>		$2\nu_3=2622$ (<i>A</i> ₁) (CHDN ₂) $\nu_4+2\nu_8=2582$ (<i>A</i> ₁)
2850–3000	<i>w</i>	?	$\nu_5+\nu_7=2872$ (<i>A</i> ₁) (I) $\nu_1+\nu_4=2903$ (<i>A</i> ₁) $\nu_2+\nu_8=2932$ (<i>B</i> ₂)
<i>P</i> 3046 <i>Q</i> 3060 <i>R</i> 3072	<i>w</i>		$2\nu_3+\nu_4=3088$ (<i>A</i> ₁)

TABLE II.—Continued

cm ⁻¹	Int.	Band type	Assignment
<i>P</i> 3124 <i>Q</i> — <i>R</i> 3149	<i>w</i>		$\nu_1(a')$ (CHDN ₂) $\nu_3+2\nu_6=3133$ (<i>A</i> ₁)
<i>P</i> 3283 <i>Q</i> — <i>R</i> 3306	<i>m</i>		$\nu_2+\nu_8=3309$ (<i>A</i> ₁)
<i>P</i> 3368 <i>Q</i> — <i>R</i> 3391	<i>w</i>		$\nu_2+2\nu_4=3420$ (<i>A</i> ₁)
<i>P</i> 4159 <i>Q</i> — <i>R</i> 4181	<i>w</i>		$2\nu_2=4192$ (<i>A</i> ₁)

^a The frequencies of the absorption peaks in this region are given in Table III.

sorption bands at 765 cm⁻¹ and 1311 cm⁻¹ not present in the spectrum of CH₂N₂ (see Fig. 2); in all other regions the spectrum of this sample was identical with

TABLE III. Absorption peaks in some perpendicular type bands of CH₂N₂ and CD₂N₂.

cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹
(a) CH ₂ N ₂ from 400 to 825 cm ⁻¹			
413	512	637	729
429	516	650	739
441	525	658	746
448	528	663	750
454	533	672	755
460	538	679	763
470	547	684	770
474	557	689	777
480	573	694	789
485	586	701	801
493	597	709	809
499	615	717	825
506	622		
(b) CH ₂ N ₂ from 875 to 1325 cm ⁻¹			
890	1013	1099	1207
900	1023	1121	1215
909	1034	1127	1223
926	1043	1137	1237
950	1051	1155	1245
956	1055	1161	1260
962	1064	1175	1268
986	1067	1179	1281
1002	1085	1184	1287
1008	1091	1195	1303
(c) CH ₂ N ₂ from 2400 to 2650 cm ⁻¹			
2437	2500	2526	2570
2453	2507	2540	2587
2471	2514	2556	2599
2485			
(d) CD ₂ N ₂ from 425 to 525 cm ⁻¹			
440	460	479	498
450	470	489	507
(e) CD ₂ N ₂ from 800 to 1050 cm ⁻¹			
836	897	938	976
858	908	942	985
866	914	954	995
873	921	958	1005
881	924	962	1013
891	933	971	1027

that of pure CH_2N_2 . These bands, also observed in the spectrum of the CD_2N_2 sample above, are presumably due to CHDN_2 impurity.

Several attempts were made to observe the Raman spectrum using 5461Å excitation on solutions of CH_2N_2 in various inert solvents. Only small concentrations of CH_2N_2 were obtainable, and none of the plates showed any Raman lines which could be attributed to CH_2N_2 .

ASSIGNMENT OF FREQUENCIES

Diazomethane is a planar, nonlinear pentatomic molecule with symmetry C_{2v} . The nine normal modes of vibration and their symmetry classes are shown in Fig. 3, the totally symmetric A_1 vibrations and the anti-symmetric B_1 vibrations being drawn according to the subsequent normal-coordinate calculations. All the fundamental frequencies are theoretically active both in the infrared and in the Raman spectrum.

The contours of the infrared bands may be predicted as follows: taking the electron diffraction² values for the C—N and N—N bond lengths, *viz.*, $r_{\text{C-N}} = 1.34 \pm 0.05$ Å. U. and $r_{\text{N-N}} = 1.13 \pm 0.04$ Å. U., and assuming the C—H bond lengths to be 1.07 Å. U., as in ethylene, and the H—C—H bond angle to be 120° , the principal moments of inertia for CH_2N_2 and CD_2N_2 are:

CH_2N_2	CD_2N_2
$I_A = 2.9 \times 10^{-40}$ g cm ²	5.8×10^{-40} g cm ²
$I_B = 76.6$	86.7
$I_C = 79.5$	92.5

The molecules thus approximate very closely to symmetric tops. The type A_1 bands should show P , Q , R structures characteristic of "parallel" bands of a symmetric top, the intensity of the Q branch⁴ being considerably less than the intensity of the P and R branches, owing to the small value of I_A/I_C . The PR spacings may be calculated from the equations of Gerhard and Dennison⁵ and are found to be 25.3 cm^{-1} for CH_2N_2 and 24.3 cm^{-1} for CD_2N_2 . The observed spacing of the parallel bands is in satisfactory agreement with these calculations.

For CH_2N_2 the four parallel fundamentals are readily assigned as $\nu_1^{\text{CH}} = 3074 \text{ cm}^{-1}$, $\nu_2^{\text{NN}} = 2101 \text{ cm}^{-1}$, $\nu_3^{\text{CH}_2} = 1415 \text{ cm}^{-1}$, and $\nu_4^{\text{CN}} = 852 \text{ cm}^{-1}$. For CD_2N_2 the assignment of $\nu_2^{\text{NN}} = 2096 \text{ cm}^{-1}$ is quite clear, and the bands at 1213 cm^{-1} and 662 cm^{-1} appear to be $\nu_3^{\text{CD}_2}$ and ν_4^{CN} . The assignment of ν_1^{CD} is less certain, but by use of the product rule⁶ it appears that the most probable assignment is $\nu_1^{\text{CD}} = 2241 \text{ cm}^{-1}$.

The type B_1 and B_2 bands should resemble perpendicular bands of a spindle-shaped symmetric top.⁷ In the absence of any underlying absorption or perturbing influences, these bands should consist of series of ap-

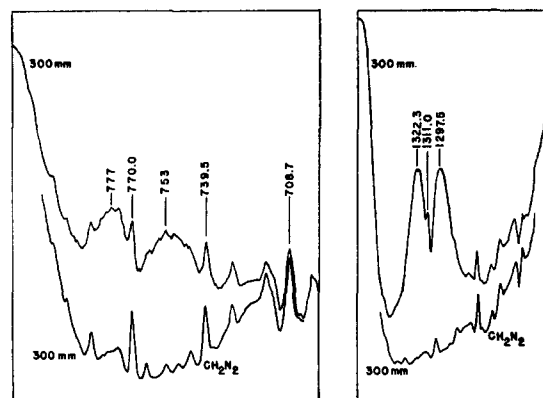


FIG. 2. The 765-cm^{-1} and 1311-cm^{-1} bands of CHDN_2 .

proximately equally spaced Q branches belonging to the various subbands present, the spacing being 18.7 cm^{-1} for CH_2N_2 and 9.1 cm^{-1} for CD_2N_2 . The intensities of the Q branches should decrease on either side of the band center according to a Boltzmann factor, approximately six or eight Q branches being observed on either side for the light molecule and about ten for the heavy molecule.

For CH_2N_2 the H nuclei follow Fermi statistics, and the ratio of the number of molecules in the even and odd K rotational levels is 1:3, respectively. An intensity alternation in the Q branches of the perpendicular bands is therefore to be expected, the first peak on the long wavelength side of the band center being the strongest one. For CD_2N_2 the D nuclei follow Bose statistics and the corresponding ratio is 2:1. For this isotope the strongest peak will be on the short wavelength side of the band center.

Several perpendicular type bands are observed in the

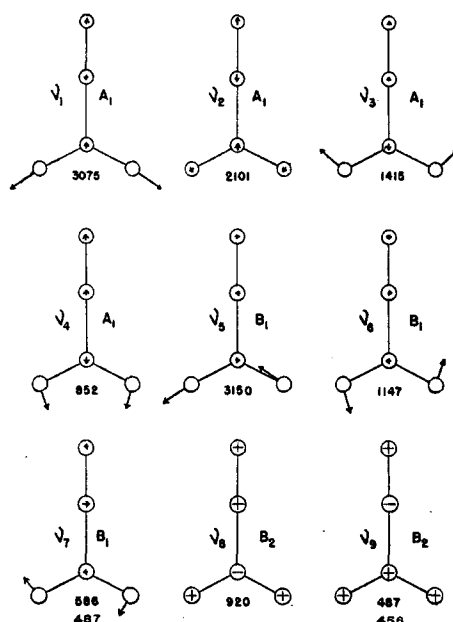


FIG. 3. Normal vibrations of CH_2N_2 .

⁴ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 421.

⁵ S. L. Gerhard and D. M. Dennison, *Phys. Rev.* **43**, 197 (1933).

⁶ E. Teller, quoted in *J. Chem. Soc.* **1936**, 966. O. Redlich, *Z. physik. Chem.* **B28**, 371 (1935).

⁷ Reference 4, pp. 424-6.

TABLE IV. Observed and calculated frequencies (cm^{-1}).

		CH_2N_2			CD_2N_2			CHDN_2		
		obs	calc	percent error	obs	calc	percent error	obs	calc	percent error
A_1 :	ν_1^{CH}	3075	3065	-0.32	2241	2238	-0.13	3137	3114	-0.73
	ν_2^{NN}	2101	2108	+0.33	2096	2091	-0.24		2104	
	$\nu_3^{\text{CH}_2}$	1415	1426	+0.78	1213	1208	-0.41	1311	1336	+1.9
	ν_4^{CN}	852	828	-2.8	662	686	+3.6	765	758	-0.93
B_1 :	ν_5^{CH}	3150	3156	+0.35	2370	2365	-0.21	2329	2299	-1.3
	$\nu_6^{\text{CH}_2}$	1147	1147	0.0	960	956	-0.42		1043 ^c	
	ν_7^{CNN}	586 ^a	577	-1.5	502 ^a	510	+1.6		534 ^c	
		487 ^b	484	-0.62	423 ^b	425	+0.47			
B_2 :	$\nu_8^{\text{CH}_2}$	920	923	+0.32	836	834	-0.24		877 ^c	
	ν_9^{CNN}	487 ^a	481	-1.2	406 ^a	410	+1.0		452 ^c	
		456 ^b	455	-0.22	382 ^b	386	+1.0			

^a Assignment I; see text.^b Assignment II; see text.^c Calculated with the force constants of Assignment I.

spectra of both CH_2N_2 and CD_2N_2 but, unfortunately, all these bands are overlapped or perturbed by neighboring absorption bands. The antisymmetric C-H and C-D stretching bands are both overlapped by strong parallel bands, only three Q branches showing in each case. The Q branch spacings, however, agree with the values expected and the intensity alternation is clearly visible in the case of the C-H stretching band. The band centers cannot be located with certainty but are tentatively assigned as $\nu_6^{\text{CH}} = 3150 \text{ cm}^{-1}$ and $\nu_6^{\text{CD}} = 2370 \text{ cm}^{-1}$.

The complex absorption below 700 cm^{-1} for CH_2N_2 is presumably caused by the two skeletal vibrations, ν_7 and ν_9 . The spacing, however, is highly irregular and probably indicates a Coriolis interaction between these two vibrations. Some indication of the positions of the band centers may be obtained from the overtones of these bands, but these are not conclusive. Indeed, two interpretations are possible, both of which seem equally reasonable. The two assignments are given below.

Two parallel bands appear to lie at 1172 cm^{-1} and 974 cm^{-1} , which may be reasonably assigned to $2\nu_7$ and $2\nu_9$, giving 586 cm^{-1} and 487 cm^{-1} as the apparent frequencies of the low-lying fundamentals (Assignment I). The alternative assignment is obtained by noting that a parallel band appears to be at 912 cm^{-1} , giving 456 cm^{-1} for one of the fundamentals. It is interesting to note that the latter frequency lies near the maximum of the absorption curve. Assigning ν_7 and ν_9 at 487 cm^{-1} and 456 cm^{-1} (Assignment II) does not explain the

apparent parallel band at 1172 cm^{-1} , but the preceding assignment does not explain the one at 912 cm^{-1} . These two assignments will be discussed in more detail later.

The absorption in the region $1050\text{--}1300 \text{ cm}^{-1}$ shows four well-defined Q branches at 1067 , 1099 , 1137 , and 1175 cm^{-1} with a marked intensity alternation and may be assigned to the CH_2 rocking motion, $\nu_6(b_1)$, or to the CH_2 wagging motion, $\nu_8(b_2)$. The former assignment is favored by the appearance of a parallel combination band with $\nu_6^{\text{CH}}(b_1)$ at 4288 cm^{-1} . This, and a parallel overtone at 2303 cm^{-1} , support the choice of 1147 cm^{-1} as the band center.

The CH_2 wagging motion, $\nu_8(b_2)$, may be assigned to the perpendicular band in the region $1050\text{--}850 \text{ cm}^{-1}$ or to the weak perpendicular band in the region $800\text{--}650 \text{ cm}^{-1}$. The former assignment is more likely because of the appearance of the parallel band, $\nu_3 + 2\nu_8$, at 3255 cm^{-1} , and this is supported by the spectrum of CD_2N_2 . The band center is difficult to locate but has been

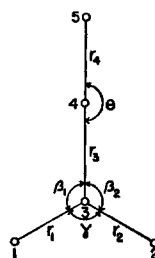
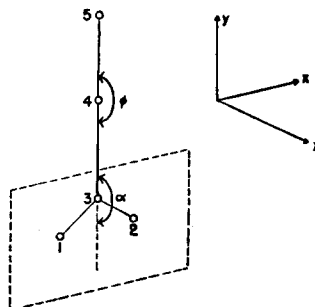


FIG. 4. Internal coordinates of diazomethane.

TABLE V. Thermodynamic functions for CH_2N_2 (hypothetical ideal gas, 1 atmos).

T $^{\circ}\text{K}$	C_p^0 cal/degree/ mole	$H^0 - E_0^0$ cal/mole	$F^0 - E_0^0$ cal/mole	S^0 cal/degree/ mole
100	8.07	797	-3892	46.89
200	9.59	1668	-8906	52.87
298.16	11.68	2711	-14,309	57.08
300	11.73	2734	-14,415	57.16
400	13.66	4006	-20,317	60.81
500	15.25	5454	-26,547	64.00
600	16.56	7046	-33,106	66.92
800	18.60	10,570	-47,014	71.98
1000	20.13	14,454	-61,862	76.32

tentatively assigned as $\nu_8^{\text{CH}} = 920 \text{ cm}^{-1}$, which is near the strong Q branch at 909 cm^{-1} .

The assignments for CD₂N₂ are more difficult. One immediately notices two parallel bands, at 765 cm^{-1} and 712 cm^{-1} , which might be overtones of the low-lying fundamentals. However, the band at 765 cm^{-1} was observed in the sample obtained in the abortive attempt to prepare CD₂N₂, while the stronger bands at 1213 cm^{-1} and 662 cm^{-1} were absent. The band at 765 cm^{-1} must, therefore, be due to CHDN₂. A few calculations with the product rule show that 356 cm^{-1} is unreasonably low for a fundamental, so we are inclined to overlook the apparent parallel band at 712 cm^{-1} . In order to find values for the skeletal bending frequencies, it was necessary to assign frequencies to the CD₂ rocking and wagging motions and then use the product rule. The perpendicular bands in the region $800\text{--}1050 \text{ cm}^{-1}$ are presumably caused by the two CD₂ motions, ν_6 and ν_8 . The band center of the former has been assigned at 960 cm^{-1} , near the peak of the absorption curve, and the band center of the latter has been set at 836 cm^{-1} .

Both of the previously mentioned assignments for ν_7 and ν_9 in CH₂N₂ were used with the above assignments for the CH₂ and CD₂ motions to calculate the values of the skeletal bending frequencies in CD₂N₂ necessary to satisfy the product rule. With $\nu_7 = 586 \text{ cm}^{-1}$ and $\nu_9 = 487 \text{ cm}^{-1}$ for CH₂N₂, the corresponding frequencies for CD₂N₂ are 502 cm^{-1} and 406 cm^{-1} . If $\nu_7 = 487 \text{ cm}^{-1}$ and $\nu_9 = 456 \text{ cm}^{-1}$ for CH₂N₂, we find 423 cm^{-1} and 382 cm^{-1} for CD₂N₂.

The complete assignments of the fundamentals and overtones for CH₂N₂ and CD₂N₂ on the basis of Assignments I and II are given in Tables I and II. The most serious objection to Assignment I is that it predicts a rather strong fundamental for CD₂N₂ at 502 cm^{-1} in a region where little absorption is observed. On the other hand, Assignment II does not give a satisfactory interpretation of the perpendicular band for CH₂N₂ in the region $650\text{--}800 \text{ cm}^{-1}$ or of the strong parallel band at 2178 cm^{-1} in the spectrum of CD₂N₂. In view of these facts, both of these proposed assignments are presented with some reserve. Unfortunately, the data available at this time do not afford a more satisfactory explanation of the observed spectra.

Supporting evidence for certain aspects of the assignment was gained by a normal-coordinate treatment and calculation of force constants. It will be noted in Table I that four bands in the spectrum of the CD₂N₂ sample (at 3137 cm^{-1} , 2329 cm^{-1} , 1311 cm^{-1} , and 765 cm^{-1}) are attributed to the presence of CHDN₂. The force constants obtained from the frequencies assigned to CH₂N₂ and CD₂N₂ were used to calculate the frequencies to be expected for CHDN₂. Satisfactory agreement was found for these four bands. While the force constants used for this were for Assignment I, it seems very probable that the set of force constants for Assignment II would give equally good results.

The observed and calculated frequencies for the three

TABLE VI. Valence force symmetry coordinates (see Fig. 4).

$S_{\text{CH}} = 2^{-1/2}(\Delta r_1 + \Delta r_2)$
$S_{\text{CN}} = \Delta r_3$
$S_{\text{NN}} = \Delta r_4$
$S_\gamma = 6^{-1/2}r_1^0(2\Delta\gamma - \Delta\beta_1 - \Delta\beta_2)$
$S'_{\text{CH}} = 2^{-1/2}(\Delta r_1 - \Delta r_2)$
$S_\beta = 2^{-1/2}r_1^0(\Delta\beta_1 - \Delta\beta_2)$
$S_\theta = r_3^0\Delta\theta$
$S_\phi = r_3^0\Delta\phi$
$S_\alpha = r_3^0\Delta\alpha$

isotopic molecules are given in Table IV. In the A_1 group there is a discrepancy of 5.5 percent between the observed and theoretical product rule ratios. In the B_1 and B_2 groups the values taken for ν_7 and ν_9 in CD₂N₂ were about 1 percent less than the calculated values.

The thermodynamic functions for CH₂N₂ have been calculated for a number of temperatures on the basis of Assignment I and are given in Table V. The values of the constants given in the tables of the American Petroleum Institute, Project 44 (December 31, 1947), were used for these calculations. The vibrational contributions were obtained from the tables given in Taylor and Glasstone's *Treatise on Physical Chemistry*, Vol. I. If Assignment II is preferred, the corrections to be added vary from $0.03\text{--}0.33 \text{ cal/degree mole}$ for C_p^0 , $0\text{--}140 \text{ cal/mole}$ for $H^0 - E_0^0$, $0\text{--}300 \text{ cal/mole}$ for $F^0 - E_0^0$, and $0\text{--}0.44 \text{ cal/mole degree}$ for S^0 .

$A_1 :$	S_{CH}	S_{CN}	S_{NN}	S_γ
S_{CH}	$\mu_c + A\mu_c$	$2^{1/2}\eta\mu_c$	0	$-3^{1/2}\sigma\mu_c$
S_{CN}		$\mu_c + \mu_N$	$-\mu_N$	$-6^{1/2}D\mu_c$
S_{NN}			$2\mu_N$	0
S_γ				$3\mu_c + 3B\mu_c$

$B_1 :$	S'_{CH}	S_β	S_θ
S'_{CH}	$\mu_c + B\mu_c$	$-bB\mu_c$	$-B^{1/2}\mu_c$
S_β		$\mu_c + a^2B\mu_N + b^2B\mu_c$	$B^{1/2}b\mu_c + B^{1/2}a(1+p)\mu_N$
S_θ			$\mu_c + (2p^2 + 2p + 1)\mu_N$

$B_2 :$	S_β	S_α
S_β	$\mu_c + (2p^2 + 2p + 1)\mu_N$	$-(1+q)\mu_c - (1+p)\mu_N$
S_α		$(q^2/2)\mu_c + (1+q)^2\mu_c + \mu_N$

The symbols have the following meanings (Fig. 4):

$$\begin{aligned} \mu_c &= \frac{1}{2} \left(\frac{1}{m_1} \pm \frac{1}{m_2} \right) & A &= 1 + \cos \gamma \\ \mu_c, \mu_N &= \frac{1}{m_c}, \frac{1}{m_N} & B &= 1 - \cos \gamma \\ \eta &= \cos \beta & D &= \cos \beta \tan(\frac{1}{2}\gamma) \\ \sigma &= \sin \beta & p &= r_2^0/r_3^0 \\ a &= r_1^0/r_3^0 \sin \beta & q &= r_2^0/r_1^0 \cos(\frac{1}{2}\gamma) \\ b &= a - \cot \beta \end{aligned}$$

FIG. 5. G matrix elements for CH₂N₂ and CD₂N₂.

A_1 :	S_{CH}	S_{CN}	S_{NN}	S_γ
S_{CH}	K'_{CH}	0	0	0
S_{CN}		K_{CN}	k_{CN}^{NN}	l_γ^{CN}
S_{NN}			K_{NN}	0
S_γ				H'_γ

B_1 :	S'_{CH}	S_β	S_θ
S'_{CH}	K''_{CH}	0	0
S_β		H'_β	$h_{\beta\theta}$
S_θ			H_θ

B_2 :	S_β	S_α
S_β	H_β	$h_{\beta\alpha}$
S_α		H_α

FIG. 6. F Matrix for diazomethane.

NORMAL COORDINATE TREATMENT

The secular equations were set up by the \mathfrak{F} and \mathfrak{G} matrix method of Wilson.⁸ The internal coordinates are shown in Fig. 4. The valence-force symmetry coordinates (VFSC) used in forming the irreducible representations of the point group C_{2v} are given in Table VI. These were chosen to be orthogonal to the redundancy involving the angles β_1 , β_2 , and γ . Those coordinates involving angles were defined as the product of the angular displacement and the equilibrium length of an adjacent bond so all force constants would have the same dimensions.

The \mathfrak{G} matrix for the VFSC is given in Fig. 5. The blocks given utilize the symmetry factoring for the point group C_{2v} . In the case of $CHDN_2$, point group C_s , the A_1 and B_1 blocks are connected by two interaction terms: between $S_{CH}(A_1)$ and $S'_{CH}(B_1)$ we have $\mathfrak{G}_{CH,CH'} = \mu_-/2$, and between $S_\gamma(A_1)$ and $S_\beta(B_1)$ we have $\mathfrak{G}_{\gamma\beta} = -3^{\frac{1}{2}}\mu_-/2$.

The \mathfrak{F} matrix ($2V = \tilde{S}\mathfrak{F}S$) is given in Fig. 6. The only interaction terms which were discarded were those involving C—H or C—D stretching motions, and the one involving the N—N stretching and the CH_2 or CD_2 deformation, the last being omitted because these two groups do not have an atom in common.⁹

The force constants were obtained from the secular equations by the usual algebraic methods. Since the

TABLE VII. Force constants for diazomethane, 10^6 dynes/cm.

Force constant	Assignment	
	I	II
K'_{CH} (C—H stretch)	5.32	same
K_{NN} (N—N stretch)	17.75	same
K_{CN} (C—N stretch)	5.11	same
H'_γ (CH_2 deformation)	0.290	same
k_{CN}^{NN} (interaction)	0.94	same
l_γ^{CN} (interaction)	0.25	same
$K_{CH''}$ (C—H stretch)	5.23	same
H'_β (in-plane CH_2 rocking)	0.518	0.481
H_θ (in-plane CNN bend)	0.503	0.401
$h_{\beta\theta'}$ (interaction)	0.04	0.107
H_ϕ (out-of-plane CNN bend)	0.451	0.435
H_α (out-of-plane CH_2 wag)	0.083	0.079
$h_{\phi\alpha}$ (interaction)	-0.058	-0.065

algebraic equations obtained from the observed frequencies are somewhat inconsistent, least-square treatments were used to get better sets of force constants for the A_1 and B_1 groups. The force-constant sets obtained from the two assignments are given in Table VII.

The pairs of frequencies, 586 cm^{-1} and 487 cm^{-1} , and 487 cm^{-1} and 456 cm^{-1} , were assigned to species B_1 and B_2 , respectively. The reverse assignment was considered in both cases, but this leads to less satisfactory sets of force constants. H_θ and H_ϕ might be expected to have similar magnitudes, and this is more nearly true for the assignments chosen than for the reverse ones.

The unsymmetric molecule, $CHDN_2$, belongs to point group C_s and, therefore, has seven vibrations in the totally symmetric species. The roots of this seventh-order secular equation were found by forming the $\mathfrak{G}\mathfrak{F}$ product and then applying an iteration process.¹⁰

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⁹ B. L. Crawford, Jr. and S. R. Brinkley, J. Chem. Phys. **9**, 69 (1941).

¹⁰ Frazer, Duncan, and Collar, *Elementary Matrices* (The MacMillan Company, New York, 1947), pp. 142-5.