although his model is undoubtedly too simple. Pound[10] has found that in order to account for the temperature dependence of the frequencies in solid I_2, it is necessary to consider intermolecular bonding as proposed by Townes and Dailey,[4] as well as the effect of the thermal motion of the molecules as proposed by Bayer.

It has been pointed out[11-13] that values of the coupling constant obtained from pure quadrupole spectra of solids may differ by as much as 10% from the values for the same molecule obtained from microwave investigations of the gases. Thus extreme care must be exercised in interpreting these solid state values in terms of molecular bonding. The increase in the absorption frequency observed as acetic acid is successively chlorinated roughly parallels the increases observed in the corresponding chlorinated methanes.[11] If it is assumed that the frequency change from compound to compound is due to the different electron withdrawing power of substituent groups, then by considering the trichloro compounds it is found that the withdrawal effect increases in the order: $-CH(OH)_2$, $-CONH_2$, $-COOH$, $-COCl$. A longer series of substituent electron withdrawal effects can be deduced from the monochloro substituted series of compounds. The observed frequencies in this series indicates that the electron withdrawal ability increases in the order $-COO^-$, $-CONH_2$, $-COCH_3$, $-COCH_2Cl$, $-COOC_2H_5$, COOH. These series are both in agreement with those obtained on the basis of chemical evidence alone.

Further evidence for this order comes from the shifts of the carbonyl stretching frequencies in the infrared spectra of these compounds. The carbonyl stretching frequency is presumably related in some way to the charge on the carbon atom of this group. The same residual charge determines the electron withdrawal effect in these series of compounds, hence one might expect a correlation between the observed quadrupole coupling constants and the frequency of the carbonyl stretching frequency in these compounds. Unfortunately these frequencies are not available for all these chlorinated compounds, but if we consider the analogous non-chlorinated compounds[14] it is found that the $C{=}O$ infrared frequencies increase in the same order as the coupling constants. The carbonyl frequency of chloroacetone could not be found in the literature; however, a measurement shows this frequency to be slightly higher in chloroacetone than in acetone as might have been predicted.

From this evidence it would seem that either the solid state effects are relatively constant in this series or they do not differ enough to invert the order of these series. The correlation of solid-state quadrupole-coupling constants with Hammett's σ for a series of substituted benzenes[15] seems to lend additional support to this hypothesis.

Acknowledgment.—The author wishes to thank Professor E. Bright Wilson, Jr., for many helpful discussions during the course of this work. He is also indebted to Messrs. L. Hedrick, H. Meal, G. Jones and C. Dean for extensive help on the instrumentation.

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[CONTRIBUTION FROM CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Infrared Spectra and Structure of the Chloramines and Nitrogen Trichloride[1]

BY GORDON E. MOORE AND RICHARD M. BADGER

RECEIVED JUNE 9, 1952

The infrared vibration–rotation spectra of gaseous NH_2Cl, NHDCl, $NDCl_2$ and NCl_3 were investigated from 1.4 to 25μ. Several fundamental vibrations were identified, and the large rotational constants were evaluated for NH_2Cl, NHDCl and $NHCl_2$. With the assistance of reasonable assumptions regarding other parameters these were used to calculate an H–N–Cl angle of 102° in NH_2Cl, and suggest that $\angle$Cl–N–Cl = 106° and r_{N-Cl} = 1.76 Å. in $NHCl_2$. These parameters are interpreted on the basis of simple electronic considerations.

Introduction

The chloramines may be regarded as ammonia with one or more of the hydrogen atoms substituted by chlorine. While they have been known for a long time,[2] only the completely substituted compound NCl_3 has been investigated extensively. However, as far as we are aware, even its structural parameters have never been determined. Information concerning the properties of dichloramine is particularly lacking. The reason for this lack of experimental data probably lies in the instability of these compounds. Both mono- and dichloramine decompose readily to yield, among other products, the sensitive and powerful explosive nitrogen trichloride.

Since these molecules presumably have a rather simple structure, it was felt that a study of their infrared vibration–rotation spectra should allow one to draw some conclusions regarding their molecular configuration.

Experimental

Samples were prepared by reaction of aqueous NH_3 and NaOCl at 0°. The resulting solution was warmed to 15–25° and connected through a $CaCl_2$ filled drying tower to an evacuated cell. After nearly every preparation it was necessary to cleanse the entire system and replace the desic-

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(1) Contribution No. 1696 from the Gates and Crellin Laboratories of Chemistry.

(2) For a good review of their chemistry see J. F. T. Berliner, *J. Am. Water Works Assoc.*, **23**, 1320 (1931).

TABLE I

VIBRATIONAL FREQUENCIES OBSERVED FOR THE CHLORAMINES

Cm.$^{-1}$	I^a	Assignment	Cm.$^{-1}$	I^a	Assignment	Cm.$^{-1}$	I^a	Assignment
	NH_2Cl			$NHCl_2$			NCl_3	
6522.9	M	$\nu_1 + \nu_5$ (A″)	6393.9	M	$2\nu_1$ (A')	1273	W	2(N–Cl stretch)
4893.8	M	$\nu_2 + \nu_5$ (A″)	3279.0	VS	ν_1 (a')(N–H stretch)	1021	W	(Stretch + bend)
3380.0	S	ν_5 (a″)(assym. N–H stretch)	2584	W	$2\nu_5$ (A')	652	S	N–Cl stretch
2020	W	$2\nu_3$ (A')	1960	W	$2\nu_2$ (A')	~390^c	?	Bend
1553	S	ν_2 (a')(NH_2 "scissors" bend)	1295	M	ν_5 (a″)(H bend out of plane)		NHDCl	
1032	VS	ν_3 (a')(H_2N–Cl bend)	1002	VS	ν_2 (a')(H bend in plane)			
686	VW	ν_4 (a')(N–Cl stretch)	687^b	S	ν_3 (a')(sym. N–Cl stretch)	3339.1	S	(N–H stretch)
			666^b	S	ν_6 (a″)(asym. N–Cl stretch)	2490	M	(N–D stretch)

^{a} Intensity: VS, very strong; S, strong; M, medium; W, weak; VW, very weak. ^{b} Maxima, but probably not band centers. ^{c} Absorption increasing at 400 cm.$^{-1}$ cut off of KBr prism.

cant since traces of products from previous preparations appeared to act as catalysts for the decomposition. The gas collected in the cell contained some mixture of NH_3, NH_2Cl, $NHCl_2$ and NCl_3 as well as some N_2 and occasionally a little N_2O. The exact composition of the mixture depended on the ratio of NH_3 to NaOCl and the *p*H of the solution. In general more NaOCl and lower *p*H favored the more highly chlorinated products.

First attempts to prepare half-deuterated chloramine by distilling from a solution containing about 50% heavy water were completely unsuccessful. The chloramine and ammonia collecting in the absorption cell were undeuterated. This was probably due to a very rapid exchange between hydrogen in the chloramine and ammonia and that in water remaining in the desiccant. This rapid exchange proved to offer a very effective method for preparing heavy chloramine.

In the second method the desiccant was thoroughly baked out under vacuum and a few tenths of a milliliter of D_2O (99.8%) were added to the top of the drying column and heated to disperse it throughout the $CaCl_2$. An ordinary mixture of ammonia and hypochlorous acid was then distilled through the deuterium treated $CaCl_2$ and the gases collected in an absorption cell in the usual manner. Good exchange took place and the collected gases were rich in deuterated compounds. Since our primary interest was in the half-deuterated monochloramine NHDCl, only a small quantity of heavy water was employed.

Mixtures of ammonia and monochloramine were quite stable and could be investigated for about two hours before decomposition became troublesome. Unfortunately the bands of these two compounds strongly overlap one another, making measurements difficult. Samples containing only NH_2Cl or a mixture of NH_2Cl and $NHCl_2$ decomposed autocatalytically shortly after their preparation. For a typical sample decomposition was first noticed seven minutes after preparation and 45 seconds later was essentially complete. No such sample persisted more than 20 minutes. This decomposition necessitated observing several bands in sections. Samples containing the most $NHCl_2$ were the shortest lived. We were not able to observe the spectrum of $NHCl_2$ without considerable NH_2Cl present. While ammonia inhibits the decomposition of NH_2Cl, it seems to react rapidly with $NHCl_2$. Accordingly no samples containing $NHCl_2$ in the presence of NH_3 were obtained. Nitrogen trichloride was observed primarily as a decomposition product from the samples rich in $NHCl_2$. Samples of NCl_3 decomposed quite slowly and could be investigated for well over an hour.

Three spectrographs were employed to investigate the spectra. A Beckman IR-2 spectrophotometer was used in the rock salt region. A vacuum prism instrument with KBr optics was used from 12 to 25 μ.[3] The region from 1.4 to 3.2 μ was investigated under high dispersion with a vacuum grating spectrograph[4] employing a 7500 lines/inch replica grating. Lines in the 1.4 and 1.9 μ water bands[5] in the first and second orders were used for calibration. Frequencies measured with the grating instrument are probably accurate to 0.3 cm.$^{-1}$. Relative frequencies of closely adjacent lines should be considerably more accurate.

Results

The prismatic spectra obtained for NH_2Cl, $NHCl_2$ and NCl_3 reduced to per cent. absorption, are shown in Fig. 1. Bands observed with the grating as well as one prismatic band near 10 μ are shown in Figs. 2–6. The frequencies of all band centers observed for these molecules together with their vibrational assignment appear in Table I. Measured frequencies of sub-bands for several bands of NH_2Cl and one band of NHDCl and the corresponding rotational assignments are given in Table II. Similar information for one band of $NHCl_2$ appears in Table III.

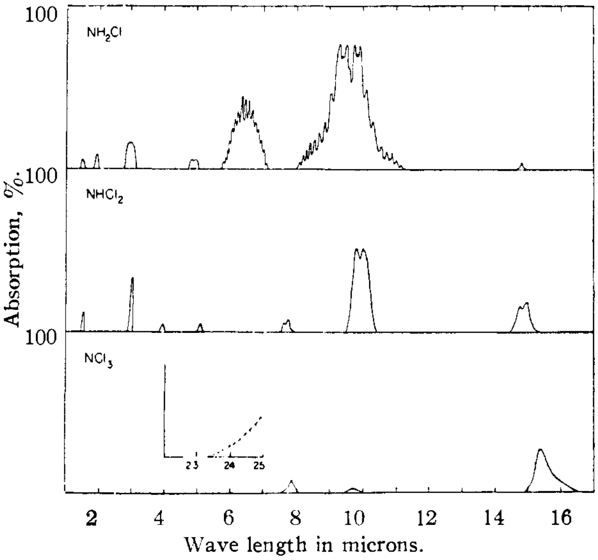

Fig. 1.—Prismatic spectra of NH_2Cl, $NHCl_2$ and NCl_3 reduced to per cent. absorption: path lengths 80 cm.; total pressure, 10 cm. in each case; partial pressures unknown.

Vibrational Assignments

A non-planar tetratomic molecule of point group C_S(NH_2Cl, $NHCl_2$) has four fundamental vibrations symmetric with respect to the symmetry plane of the molecule (a') and two anti-symmetric with respect to this plane (a″). For the molecules under consideration these will be designated as in Table I.

NH_2Cl.—The bands of NH_2Cl should be of two types which should be more or less easily distinguishable. The a″ fundamentals should be of

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[3] This instrument was a gift from the Shell Development Company. For a description see R. R. Brattain, *Phys. Rev.*, **60**, 164 (1941).

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[5] R. C. Nelson, Summary Report No. IV, Contract NObs 28373, Dept. Physics, Northwestern University.

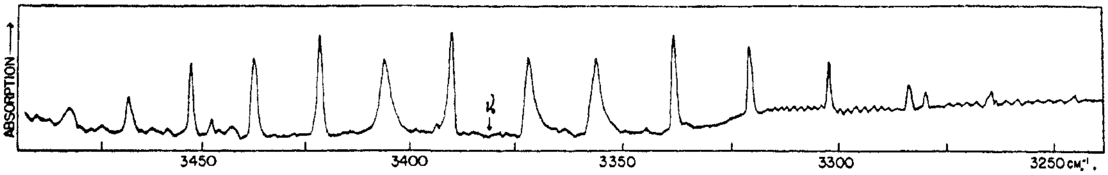

Fig. 2.—ν_5 of NH_2Cl: ν_1 of $NHCl_2$ shows weakly at low frequency end of tracing; path length 80 cm.; total pressure, 10 cm.; maximum absorption is about 45%.

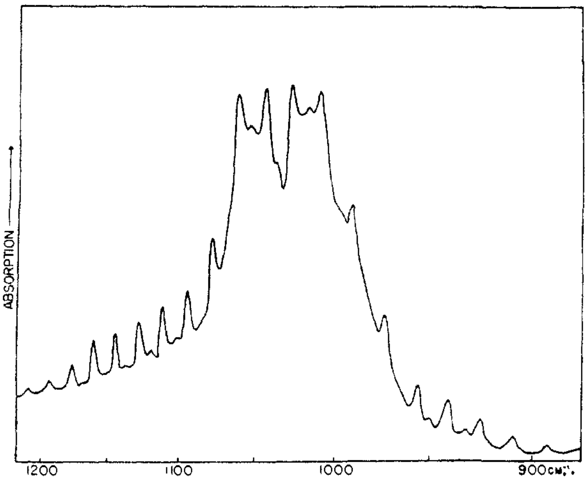

Fig. 3.—ν_3 of NH_2Cl: weaker maxima are probably NH_2Cl^{37}; path length 80 cm.; total pressure, 10 cm.; maximum absorption is about 85%.

pure B or "perpendicular" type without central Q branch, while the a′ modes should give rise to hybrid A, C bands. The latter need not exhibit an obvious central branch, but may be expected to show a concentration of unresolved absorption on both sides of the band center.

In the region of the N–H valence fundamentals only one band was observed (Fig. 2). This has its center at 3380 cm.$^{-1}$ and must be assigned to ν_5 because of its pure perpendicular character. The assignments of the bands at 1553 cm.$^{-1}$ and at 1032 cm.$^{-1}$ to the NH_2 "scissors" mode and the H_2N–Cl band, respectively, is very plausible on the basis of frequency and band type. The latter assignment is further supported by the chlorine isotope shift, which would be expected to be appreciable for this vibration, though negligible for ν_2. The 1032-cm.$^{-1}$ band (Fig. 3) possesses a weak satellite with center at 1024 cm.$^{-1}$ which we attribute to the molecule NH_2Cl^{37}. Though complete data are lacking for application of the product rule, qualitative considerations show that the observed shift of 8 cm.$^{-1}$ is within the range to be expected.

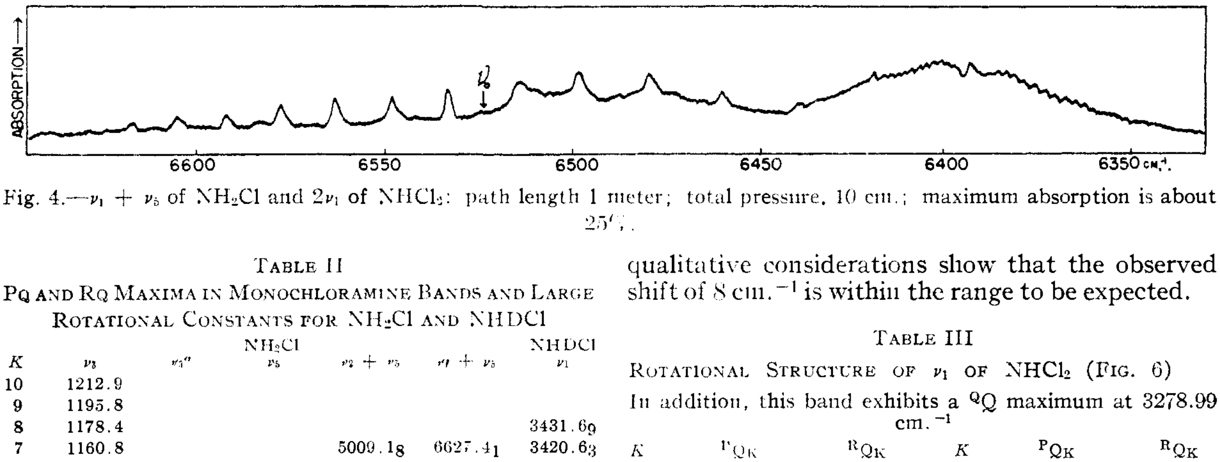

Fig. 4.—$\nu_1 + \nu_5$ of NH_2Cl and $2\nu_1$ of $NHCl_2$: path length 1 meter; total pressure, 10 cm.; maximum absorption is about 25%.

TABLE II

PQ AND RQ MAXIMA IN MONOCHLORAMINE BANDS AND LARGE ROTATIONAL CONSTANTS FOR NH_2Cl AND NHDCl

	NH_2Cl					NHDCl
K	ν_3	$\nu_3{}^a$	ν_5	$\nu_2 + \nu_5$	$\nu_1 + \nu_5$	ν_1
10	1212.9					
9	1195.8					
8	1178.4					3431.6_9
7	1160.8			5009.1_8	6627.4_1	3420.6_3
6	1143.3		3482.9_2	4995.2_7	6615.3_5	3410.1_0
5	1127.4		3468.4_0	4980.4_4	6602.8_0	3399.4_6
4	1110.8	1100.1	3452.8_2	4965.9_5	6589.9_7	3388.7_6
3	1093.4	1082.4	3437.1_5	4950.2_2	6575.1_9	3378.2_3
2	1075.8	1066.2	3421.1_4	4934.8_3	6560.5_9	3367.4_0
1	1058.2	1050.4	3405.3_5	4919.0_1	6545.6_5	3356.5_4
0	1040.3	1033.4	3388.8_9	4902.9_7	6530.0_1	3345.7_5
1	1023.9	1014.7	3370.9_5	4884.7_4	6511.6_7	3333.1_5
2	1006.2	995.8	3354.4_8	4868.8_3	6495.6_9	3322.8_6
3	989.3	979.0	3336.6_6	4850.0_9	6476.7_0	3309.5_6
4	972.0		3318.6_5	4832.3_1	6457.6_3	3297.4_1
5	955.6		3300.7_6	4813.9_6	6438.7_9	3285.0_3
6	937.9		3282.5_1	4795.4_4	6419.2_0	3272.8_6
7	922.8		3263.9_8	4776.3_4	6398.1_0	3260.0_5
8	907.4		3245.2_8	4757.2_2		3247.4_4
9	893.3					

$$A'' - \frac{1}{2}(B'' + C'') = 8.56 \pm 0.01 \text{ cm.}^{-1} \text{ for } NH_2Cl^b$$
$$= 5.83 \pm 0.01 \text{ cm.}^{-1} \text{ for } NHDCl^c$$

[a] For the isotopic molecule NH_2Cl^{37}. [b] Best extrapolated value from ν_5, $\nu_2 + \nu_5$ and $\nu_1 + \nu_5$. [c] Best extrapolated value from ν_1.

TABLE III

ROTATIONAL STRUCTURE OF ν_1 OF $NHCl_2$ (FIG. 6)

In addition, this band exhibits a ^QQ maximum at 3278.99 cm.$^{-1}$

K	^PQ_K	^RQ_K	K	^PQ_K	^RQ_K
1			12	3253.5_2	3304.1_9
2		3284.1_9	13	3251.2_3	3306.0_7
3	3273.6_4	3286.2_4	14	3248.8_1	3307.9_2
4	3271.6_7	3288.2_6	15	3246.4_8	3309.6_2
5	3269.4_1	3290.3_5	16	3244.2_8	3311.5_3
6	3267.1_9	3292.2_8	17	3241.8_5	3313.2_8
7	3264.9_2	3294.3_5	18	3239.4_3	.....
8	3262.6_6	3296.4_4	19	3237.0_2	3316.7_8
9	3260.3_7	3298.4_8	20	3234.6_0	.....
10	3257.9_7	.....	21	3232.1_7	.....
11	3255.7_6	3302.3_4	22	3229.7_5	.....

$$A'' - \frac{1}{2}(B'' + C'') = 1.072 \pm 0.002 \text{ cm.}^{-1a}$$

[a] Best extrapolated value.

The weak band at 686 cm.$^{-1}$ appears as a single line which we interpret as a central Q branch. On the basis of type and frequency we assign the

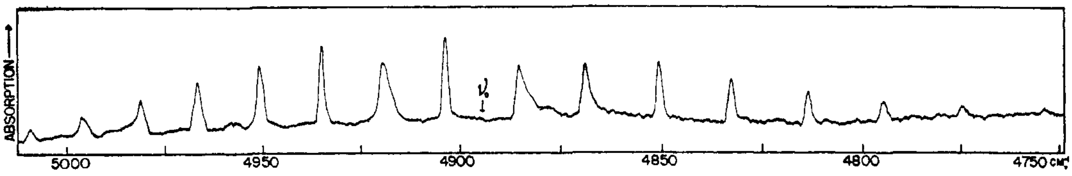

Fig. 5.—$\nu_2 + \nu_5$ of NH_2Cl: path length 1 meter; total pressure, 10 cm.; maximum absorption is about 20%.

band to the N–Cl stretch. Both $NHCl_2$ and NCl_3 show bands in this region. The failure to observe the corresponding band of NH_2Cl^{37} we attribute to its very low intensity and to interference by the CO_2 maximum at 667 cm.$^{-1}$.

We have not observed any band ascribable to ν_6, the NH_2 twist.

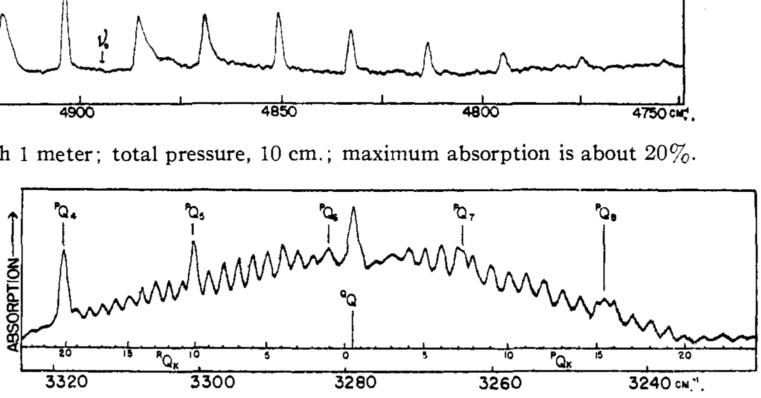

Fig. 6.—ν_1 of $NHCl_2$: maxima numbered on top are part of ν_5 of NH_2Cl; path length 80 cm.; total pressure, 10 cm.; maximum absorption is about 55%.

The few combination and overtone bands observed lend themselves to a plausible assignment. The band at 6337.4 cm.$^{-1}$ (Fig. 4) is apparently of perpendicular type and is assigned to $\nu_1 + \nu_6$. We cannot explain a seemingly real, unresolved absorption underlying the P branch of this band. Its unsymmetric disposal with respect to the major band appears to rule out the possibility that it is a parallel type component of the latter.

The perpendicular band at 4893.8 cm.$^{-1}$ is plausibly assigned to $\nu_2 + \nu_5$ and the remaining band at 2020 cm.$^{-1}$ corresponds to $2\nu_3$ with a convergence constant of 22 cm.$^{-1}$.

$NHCl_2$.—In assigning the bands of $NHCl_2$ comparison with NH_2Cl was of considerable assistance. The band at 3279.0 cm.$^{-1}$ (Fig. 6) is certainly ν_1. Its coarse rotational structure corresponds to that of a type C band, and ν_1 should have a strong component parallel to the axis of greatest inertia. Its overtone $2\nu_1$ at 6393.9 cm.$^{-1}$ is also readily identified.

The bands at 1295 cm.$^{-1}$ and 1002 cm.$^{-1}$ are believed to represent the a″ and a′ hydrogen bending modes ν_5 and ν_2, respectively. The first overtone is also observed in each case.

The region near 670 cm.$^{-1}$ shows two maxima at 687 and 666 cm.$^{-1}$, but from the observed envelope we were unable to establish a band center. It is probable that both N–Cl stretching vibrations fall in this region, and we believe the observed absorption represents a superposition of these two bands. The bending vibration ν_4 is probably outside the spectral region investigated.

NCl_3.—Though NCl_3 has two stretching vibrations, only one maximum was observed near 650 cm.$^{-1}$, a broad peak at 652 cm.$^{-1}$. The contour of this band indicates that it is not simple. An overtone corresponding to nearly twice this frequency is observed at 1273 cm.$^{-1}$.

At the long wave length end of the accessible spectrum there is some indication that another absorption is starting; conceivably this is where the bending vibrations will appear. A weak band at about 1021 cm.$^{-1}$ might be a combination of bending and stretching.

Rotational Structure

Since NH_2Cl and NHDCl are so nearly symmetrical tops, the bands observed with the grating, all of perpendicular type, show no very obvious center. The only indication of asymmetry of the rotors is the broadening of the $^RQ_1$, $^PQ_1$ and $^PQ_2$ maxima, which were very similar in all bands. The cause of the relative sharpness of the $^RQ_0$ maxima in each case is not immediately obvious.

The numbering of the lines was first accomplished by the use of intensities at the extremes of the bands, though in the case of NH_2Cl further assistance was given by the known rotational constant for the ground state obtained from ν_3, which has a well defined center. The numbering given appears to receive support from the pattern of three diffuse and one sharp line observed about each band center.

Since the rotational stretching of the chloramines is quite appreciable, the rotational constants for the rotationless state was obtained by extrapolation to $K = 0$ of plots of $[^RQ(K-1) - {}^PQ(K+1)]/(4K)$, and of $[^RQ(K) - {}^PQ(K)]/(4K)$ *versus* K^2. In the case of NH_2Cl and NHDCl, since the points on these plots scattered somewhat more than should be expected from the apparent precision of the frequency measurements, the slopes of the plots were estimated with the use of the force constants found for NH_3 and the best straight lines drawn through the points. In the case of $NHCl_2$ the effect of asymmetry is appreciable in the lower rotational levels and only levels with $K > 8$ were used to obtain the rotation constants. The best values for the constants are given in Tables II and III.

Structural Considerations

If some of the four parameters necessary to specify the structure of NH_2Cl or $NHCl_2$ can be estimated by comparison with similar compounds of known structure, one can use the experimental rotational constants to calculate the others. The large rotational constants of the isotopic molecules NH_2Cl and NHDCl are determined primarily by the N–H (and N–D) distance and the H–N–Cl angle. Accordingly, the other two parameters have been estimated and pairs of values of the N–H distance and the H–N–Cl angle were calculated.

Electron diffraction measurements give the N–Cl bond distance in $(CH_3)_2NCl$ as 1.77 ± 0.02 Å.[6,7] Since such information on monochloramine itself is lacking, the N–Cl distance is assumed the same as in the dimethyl compound. In other cases substitution of methyl groups for hydrogen atoms does not affect bond distances; for example, replacement of all three hydrogen atoms in CH_3Cl by methyl groups leaves the C–Cl distance unchanged within experimental error.[8,9]

The H–N–H angle is taken as 106°47′ as in ammonia.[10] While one can use the pair of rotational constants to restrict this angle to 103 ± 6°, the angle taken from NH_3 is preferred on the basis of arguments advanced later in this paper. Since the rotational constants are some five times as sensitive to the H–N–Cl angle, a few degrees in the H–N–H angle has relatively little effect on the values calculated for other parameters.

Figure 7 shows the pairs of values of the H–N–Cl angle and N–H distance compatible with rotational constants for both NH_2Cl and NHDCl and the assumed values for the N–Cl distance and H–N–H angle. The fact that the same set of parameters fits both rotational constants indicates that perturbations such as coriolis interaction are negligible in the vibrational bands used to obtain the constants.

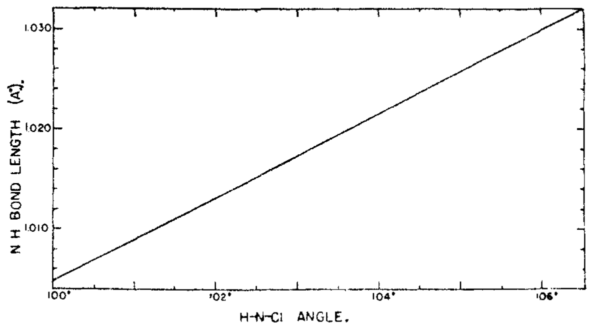

Fig. 7.—r_{N-H} against <H–N–Cl consistent with rotational constants for NH_2Cl and NHDCl: r_{N-Cl} = 1.76 Å. and <H–N–H = 106°47′.

Reference to Fig. 7 shows that for a N–H distance of 1.014 Å. as found in ammonia[10] the corresponding H–N–Cl angle is very nearly 102°. Since the asymmetric N–H stretching frequency in NH_2Cl of 3380.1 cm.$^{-1}$ is not very different from the 3414 cm.$^{-1}$ suggested for ν_3 in NH_3,[11] we feel that the N–H distances in the two molecules are nearly identical. Consequently, the H–N–Cl angle in NH_2Cl is probably 102 ± 1°.

For dichloramine the large rotational constant is determined primarily by the N–Cl distance and the Cl–N–Cl angle. By assuming the N–H distance and H–N–Cl angle to be 1.014 Å. and 102° as in NH_2Cl, one obtains the pairs of values for the other parameters given by the upper curve in Fig. 8. Since the dependence of the rotational constant on the H–N–Cl angle is appreciable, curves are plotted for two different angles. The constant is affected only very slightly by small changes in the assumed N–H distance. The curves pass near the shaded region in Fig. 8 allowed for these parameters by electron diffraction on methyl dichloramine.[5] At the point in best agreement with the electron diffraction data, 1.76 Å. and 106° for the N–Cl distance and the Cl–N–Cl angle, the non-bonded Cl–Cl distance is the same as that measured in the methyl compound. Since this is the distance probably most accurately determined by electron diffraction, we feel that the two results are compatible.

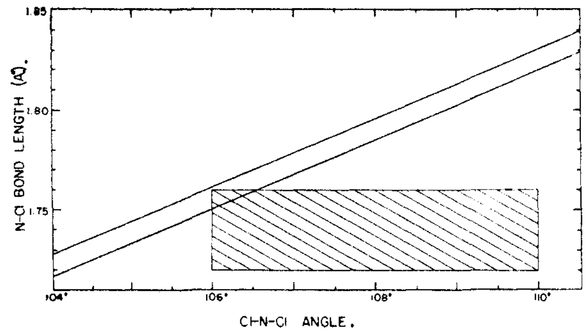

Fig. 8.—r_{N-Cl} against ∠Cl–N–Cl for $NHCl_2$: top curve, r_{N-H} = 1.014 Å., ∠H–N–Cl = 102°; bottom curve, r_{N-H} = 1.014 Å., ∠H–N–Cl = 105°. Shaded area is that allowed by electron diffraction on CH_3NCl_2.

The explanation advanced by Schomaker and Lu[12] to account for the difference in bond angles in NH_3 and NF_3 seems applicable to the chloramine. These authors suggested that the normal valence bond angle for nitrogen is about 102°. By considering the interactions of the various appended atoms with each other and with the electron pair assumed localized on the far side of the nitrogen atom they predicted how the angles should deviate from this value. Similar considerations regarding the chloramines leads one to suspect nearly normal H–N–Cl angles, while the Cl–N–Cl and H–N–H angles should be increased. The H–N–H angle in NH_2Cl should be about as large as those in NH_3. These predictions agree with our experimental results. The 102° found for the H–N–Cl angle in NH_2Cl supports Schomaker and Lu's conclusion that the normal bond angle for nitrogen is about 102°.

Acknowledgment.—We are indebted to Professor Verner Schomaker for discussions regarding structural considerations.

PASADENA 4, CALIF.

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