I. Infra-red Studies of Nitrous Acid, the Chloramines and Nitrogen Dioxide

II. Observations Concerning the Photochemical Decomposition of Nitric Oxide

Thesis

by

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ABSTRACT

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1. The results of an investigation of the infra-red spectra of gaseous nitrous acid and deutero-nitrous acid in the region to 25μ have been combined with previous data in the 1.4-15μ region to make a complete vibrational assignment. Nitrous acid exists as a pair of rotational isomers which are believed to be the cis and trans forms. The cis form is of higher energy by 500 ± 250 calories mole^{-1}. From rotational constants and by comparison of force constants with those of molecules of known structure sets of structural parameters for both species have been obtained, from which conclusions are drawn regarding the electronic structure of nitrous acid. The barrier for hindered rotation of the hydrogen atom about the nitrogen-oxygen single bond has been approximated by a three-term series, which suggests a maximum barrier height of about 12 kcal. mole^{-1}. The standard entropy of an equilibrium mixture of cis and trans nitrous acids at 25° has been calculated to be 56.0 e.u., to be compared with 54.9 e.u. and 54.8 e.u. for the pure trans and cis isomers, respectively.

2. The infra-red vibration spectra of gaseous NH_2Cl, NHDCl, $NHCl_2$ 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 $\measuredangle$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.

3. The infra-red spectrum of NO_2 has been reinvestigated in the 1.4-3.4 μ region under high dispersion. The nine bands observed show resolvable rotational structure and the moments of inertia obtained, in conjunction with the large rotational constant from measurements of ν_2 by Wilson and Brown, yield the ground state parameters $r_{N-O} = 1.188 \pm 0.004$ Å and $\measuredangle$ O-N-O = 134°4' ± 15'. The set of overtones and combinations observed together with $\nu_2 = 750.9$ cm^{-1} from Wilson and Brown allow one to determine a complete set of quadratic vibrational interaction constants. The frequencies of NO_2 are $\nu_1 = 1322.5$ cm^{-1}, $\nu_2 = 750.9$ cm^{-1} and $\nu_3 = 1616.0$ cm^{-1}. An intensity alternation is observed in type A bands as is predicted by theory but which, as far as the author is aware, has not previously been observed in a similar case. An apparently abnormal interaction which is not adequately explained occurs between the vibrational levels $3\nu_3$ and $2\nu_1 + 3\nu_2$ and likewise between $\nu_1 + 3\nu_3$ and $3\nu_1 + 3\nu_2$.

4. Section II describes briefly some experiments concerning the photochemical decomposition of nitric oxide. It was shown that absorption to the 0,0 and 1,0 γ-bands ($A^2\Sigma - X^2\Pi$) under conditions where these bands are pressure broadened leads to photochemical decomposition. Nitrogen was shown to effect the rate of decomposition only slightly when added to nitric oxide at 15 cm of Hg pressure. This decomposition is of interest because of its possible connection with the problem of the heat of dissociation of nitrogen.

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SECTION I.

A. The Infra-red Spectrum and Structure of Gaseous Nitrous Acid

INTRODUCTION

L. H. Jones (1) has studied the absorption spectrum of nitrous acid and deutero-nitrous acid from 1.4 to 15μ. His results indicate that nitrous acid exists in two stereoisomeric forms with valence formula H-O-N=O. These two coplanar structures are shown in Figure 1.

cis trans

Figure 1. Structures of nitrous acid.

Jones was able to obtain a rotational constant for one of these forms and by making certain assumptions, to draw conclusions regarding its molecular parameters. His results, however, do not lend themselves to a unique interpretation, but suggest that investigation of the spectral region to 25μ might give considerable additional information. Such is found to be the case. The results of such an investigation are presented herein together with a reinterpretation of Jones' data in the light of the new observations.

EXPERIMENTAL

The spectra beyond 15μ were recorded on a large vacuum prism spectrometer, a gift from the Shell Development Company. This instrument, described in its original form by Brattin (2), has been modified to employ an AC thermocouple detector and a servo slit-control system, as well as to include many minor changes. The servo control system is described in Appendix I. High dispersion measurements from 1.4 to 3.2 μ were made on a vacuum grating spectrometer (3) employing replica gratings of 7500 and 4500 lines per inch. The region from 1.8 to 15 μ was investigated with a Beckman IR-2 Spectrophotometer equipped for automatic recording.

Absorption cells were 50 or 100 cm in length. The 100 cm cell had fused-on glass windows, while the 50 cm cell used windows of either silver chloride or polyethylene attached to the cell with wax or glyptal resin. Alkali halide windows are rapidly attacked by the nitrous acid mixtures, making their use impractical.

Gaseous nitrous acid rapidly comes to equilibrium with its decomposition products H_2O, N_2O_3, NO and NO_2. It was therefore necessary to carry out all observations on an equilibrium mixture. For the present investigation equilibrium mixtures were prepared by two essentially different methods. Method 1, used to prepare only low pressure samples of HONO and DONO, consisted of adding a few drops of liquid water to an absorption cell that had previously been filled with nitrogen dioxide. Any nitric acid formed by the ensuing reaction remained in solution in the droplets of water, while the more volatile nitrous acid exhibited an equilibrium vapor pressure up to several mm of Hg. The principal disadvantage of this method was the relatively large equilibrium partial pressures of NO_2 and N_2O_4, both of which contribute several intense absorption bands, which in some instances overlap those of nitrous acid. This method was used for preliminary work and to check bands attributed to nitrous acid in samples prepared by the second method.

Method 2 is similar to that employed by Jones. Water vapor, oxygen and a large excess of NO were mixed in an absorption cell, normally to a total pressure of near one atmosphere. A typical mixture consisted of the equilibrium vapor pressure of water at 20°, 6mm of oxygen, and sufficient NO to give a total pressure of about 600 mm of Hg. The principal equilibria in such a mixture at room temperature are

$$NO + NO_2 = N_2O_3$$

$$N_2O_3 + H_2O = 2HONO$$

$$2NO_2 = N_2O_4 \,.$$

For this mixture one calculates from the equilibrium constants of Wayne and Yost (4) for the first two reactions and of Giauque and Kemp (5) for the third the partial pressures for the various constituents tabulated in Table I. Other mixtures yielded partial

Table I. Partial pressures of principal constituents in a mixture of 6 mm of oxygen, 17.5 mm of H_2O and 600 mm of NO.

Component	Pressure (mm of Hg)
HONO	9.3
N_2O_3	1.9
H_2O	12.8
NO_2	4.9
N_2O_4	0.36
NO	593.

pressures of nitrous acid up to 25 mm of Hg.

Since NO contributes considerably fewer absorption bands in the infra-red than do the polyatomic molecules, it is advantageous to increase the NO pressure in order to minimize the amounts of NO_2 and N_2O_4 present. Water vapor absorption, although annoying, is well known and can be subtracted out. By comparing the spectrum of the nitrous acid mixtures with that of samples prepared from only NO and oxygen, corrections can be made for the bands of N_2O_3. In only one instance does interference by N_2O_3 leave an uncertainty in the nitrous acid absorption.

Oxygen and NO_2 were taken directly from commercial cylinders without further purification. NO was prepared essentially by the method of Johnston and Giauque (6): sulfuric acid was dropped into a solution of $NaNO_2$ and KI, the evolved gas was scrubbed with 30% NaOH, then 95% H_2SO_4 and frozen in a liquid air trap. The light blue solid was held in vacuum at liquid air temperature with a mechanical pump to remove any more volatile components (N_2), then bulb-to-bulb distilled, the last 20% or so being discarded. About 90% of the retained fraction was vaporized to fill a large glass reservoir to slightly greater than atmospheric pressure. A 50 cm absorption cell filled with this NO to 600 mm pressure showed no spurious absorptions. D_2O (99.8%) was supplied under the authorization of the Atomic Energy Commission.

In order to study the changes in absorption intensities with temperature it was necessary to provide means of heating and cooling the absorption cells. Cells were heated in a tubular oven, which extended about 10 cm beyond each end of the 50 cm absorption cell. Cooling was accomplished by packing the cells in ice. All but a few centimeters of the cell's length could be cooled in this manner without condensation of atmospheric water vapor on the windows.

Since heating increases the dissociation of HONO, while cooling decreases the vapor pressure of water, it is difficult to maintain an appreciable concentration of HONO over a very large temperature range. The composition of the samples upon which the temperature study was made was chosen so that these two effects left just about equal concentrations of nitrous acid at 70° and 0° making a comparison relatively simple.

ASSIGNMENT OF VIBRATIONS

A planar form of HONO would have six vibrations which can be approximately described as in Table II. The first five of these, symmetric in the plane of the molecule, belong to symmetry class A'

Table II. Vibrations of HONO

ν_1 (A')	O-H stretching vibration
ν_2 (A')	N=O stretching vibration
ν_3 (A')	H-O-N bending in plane
ν_4 (A')	N-O stretching vibration
ν_5 (A')	O-N-O bending vibration
ν_6 (A'')	H-O-N torsional vibration (out of plane)

for the point group C_s. The last vibration, which is antisymmetric with respect to the plane, belongs to A". From the rules for multiplication, A'•A'=A', A'•A"=A", A"•A"=A', one sees that all vibrational levels not involving ν_6 an odd number of times will be symmetric in the molecular plane (A'). Transitions to these levels from the ground state have their transition moments in this plane. If the moment happens to be approximately along the axis of least inertia, one will expect type A bands, while if it is more or less perpendicular to this axis (ie., about parallel to the axis of intermediate inertia) a type B band will result. Bands involving one A" level will of necessity have their transition moments perpendicular to the plane of the molecule and will lead to type C absorptions.

Table III lists the frequencies and types of all bands observed in this investigation together with those observed by Jones. In some cases frequencies measured by Jones have been changed slightly. The spectrum beyond 15 μ for HONO is reproduced in Figure 2 and that for DONO in Figure 3. Not enough new information was obtained in the reinvestigation of the shorter wavelength region to warrant reproducing the spectra.

Bands in Table III listed as type A show only the simple PQR structure of a parallel band for a symmetric top, while the type B bands exhibit the typical ^{P}Q and ^{R}Q maxima of a perpendicular band, indicating that nitrous acid is an approximately symmetric rotor. Both the bands listed as type A and as type B exhibit the fact that they are hybrids; the former by a variable spacing between P and R branches, which is always slightly larger than that calculated from

Table III. Absorption bands of light and heavy nitrous acids.

Observed frequencies (cm^{-1}) and relative intensities				Band type	Assignment		
HONO		DONO			Jones	This work cis	trans
543.2	S	416	S	C			ν_6
598.0	VS	591.5	VS	A		- ν_5^a -	
637.5	S	507.8	S	C		ν_6	
794	VS	739*	S	A	ν_4		ν_4
856	VS	816*	VS	A	$2\nu_5$	ν_4	
1260	S	1018^{b*}	S	A	ν_3		ν_3
1292	MS					ν_3	
1696*	S	1690*	S	$-^e$	ν_2		ν_2
2505*	M			$-^e$	$2\nu_3$		$2\nu_3$
3257*	M	3196	MW	A	$\left\{\begin{array}{l}\nu_2+2\nu_4\\ 2\nu_3+\nu_4\end{array}\right.$	$2\nu_2^d$	
3372*	M	3361*	M	A	$2\nu_2$		$2\nu_2$
3426*	M	2530*	M	B	ν_1^c	ν_1	
3590*	MS	2650*	MS	A	ν_1^t		ν_1
4124*	VVW			A	$2\nu_3+\nu_2$		$2\nu_3+\nu_2$
4378*	VW			A	$\nu_1+\nu_4^t$		$\nu_1+\nu_4$
4830*	W			A	$\nu_1+\nu_3^t$		$\nu_1+\nu_3$
5038*	VW	4999*	VW	(B)	$3\nu_2$		$3\nu_2$
6050	VW			A	$\nu_1+2\nu_3^t$		$\nu_1+2\nu_3$
6664.7*	W	4963*	W	B	$2\nu_1^c$	$2\nu_1$	
7015*	W	5212*	W	A	$2\nu_1^t$		$2\nu_1$

* Frequency and relative intensity taken from Jones.
a) This band might belong to either cis or trans nitrous acid.
b) Only one band observed in this region in DONO
c) Cis species.
d) Assigned as the overtone of an unobserved fundamental.
e) Envelopes not resolved.
t) Trans species.

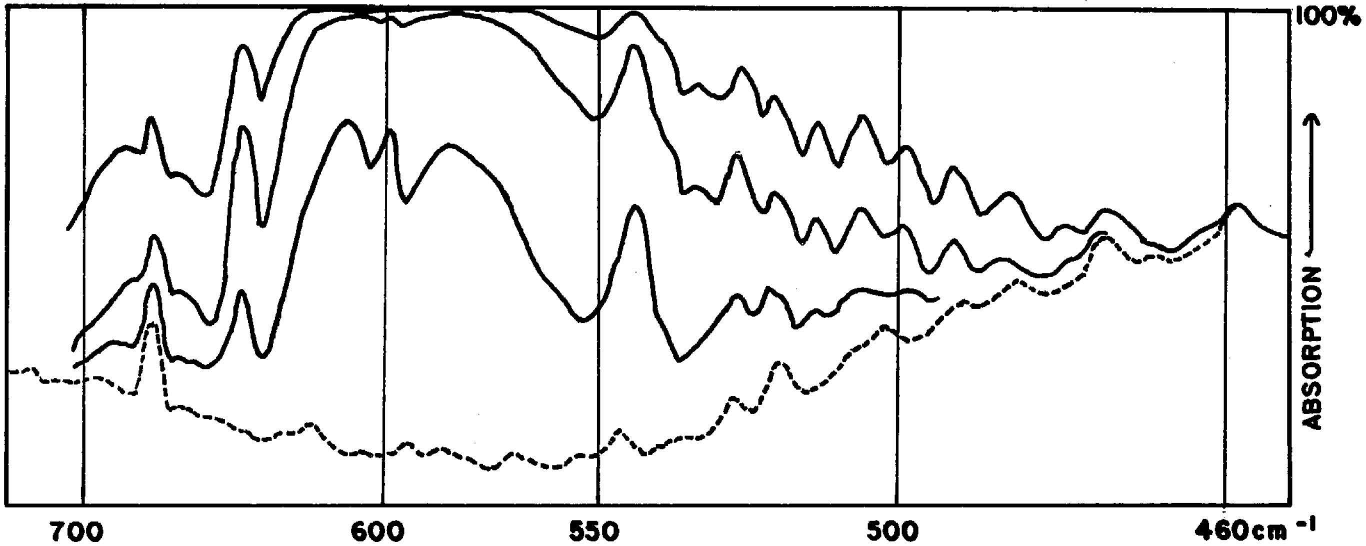


Figure 2. Spectrum of HONO in the KBr region. Path length 50 cm, partial pressures of HONO about 1.5, 5 and 10 mm of Hg.

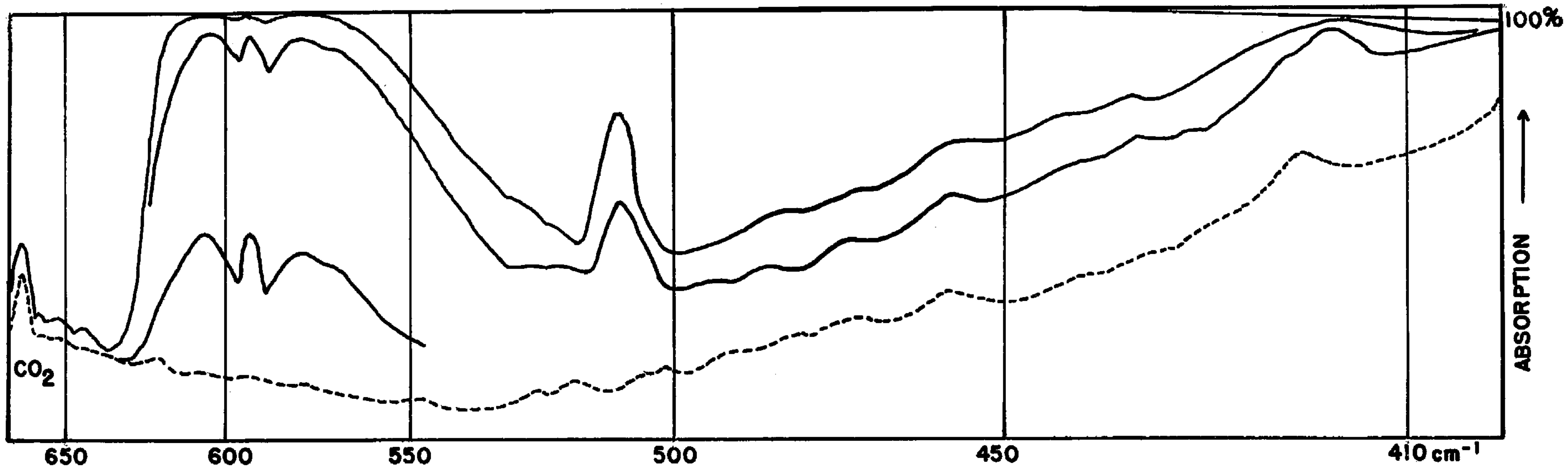


Figure 3. Spectrum of DONO in the KBr region. Path length 50 cm, partial pressures of DONO about 0.5, 3 and 6 mm of Hg.

the thermal distribution of rotational levels (7), and the latter by a more or less pronounced ^{Q}Q maximum, forbidden for a pure type B band (8). The type C bands are clearly distinguished by their very strong central maxima and the broad spacing of P and R branches. The expected rotational structure corresponding to the small moment of inertia was resolved in the P-branch of one of the type C bands, and the frequencies of these ^{P}Q maxima are listed in Table IV.

Table IV. Frequencies of subbands of ν_6-trans.

(cm^{-1})	$\Delta\nu$
536.4	
	5.6
530.8	
	7.3
523.5	
	5.8
517.7	
	6.2
511.5	
	6.1
505.4	
	6.5
498.9	
	6.5
492.4	
	6.4
486.0	
Average separation	6.4 ± 0.3

Jones' work leaves little doubt but that the spectrum must be interpreted on the basis of two different molecules of nitrous acid. While the spacings in the various bands indicate a molecule considerable lighter than a dimer of HONO, the plurality of bands clearly shows that there are more than six vibrational degrees of freedom.

Since Jones has ruled out a nitro form, $\mathrm{H{-}N}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{O}\end{smallmatrix}$, the two logical possibilities are cis and trans (see Figure 1). Only these forms will be considered. Because of his lack of data beyond 15 μ, Jones was able to assign only a few of his bands to particular vibrations of one or the other species of nitrous acid. His assignments are discussed and revised when revisions are suggested by the new observations, and all new bands are assigned.

Jones has advanced quite convincing arguments for the assignment of the bands at 3426 and 3590 cm^{-1} in HONO both as O-H stretching vibrations.

Although only one band (1696 cm^{-1}) is clearly discernible from our tracings in the N=O fundamental region, the overtone region shows two relatively strong bands at 3372 and 3257 cm^{-1}. Jones had assigned these as the overtone of the band at 1696 cm^{-1} and a ternary combination respectively. Since these two bands are among the most intense overtones and combinations observed, the assignment of the band at 3257 cm^{-1} as either $\nu_2 + 2\nu_4$ or $2\nu_3 + \nu_4$ seems open to question. Furthermore neither $\nu_2 + \nu_4$ nor $\nu_3 + \nu_4$ was observed, indicating that these vibrations do not interact strongly. A corresponding pair of bands is observed in DONO at 3361 and 3196 cm^{-1}. The relatively small isotopic shift indicates these absorptions are overtones or combinations of vibrations not involving the hydrogen atom. The assignment of the higher frequency component in each case to the overtone of the fundamentals at 1696 and 1690 cm^{-1} in HONO and DONO respectively seems quite straightforward. If the lower frequency components are considered as the overtones of the N=O stretching for the other form of nitrous acid, one calculates on the basis of about equal convergences for the cis and trans forms that the unobserved N=O stretching should occur at about 1640 cm^{-1} in HONO and 1610 cm^{-1} in DONO. Since this region is overlapped by very strong absorption from nitrogen dioxide, a band slightly less intense than the one at 1696 cm^{-1} could easily have been masked.

Jones assigned the strong bands at 1260 cm^{-1} in HONO and 1018 cm^{-1} in DONO as hydrogen bending vibrations. Although he mentioned a weaker band on the high frequency side of the one at 1260 cm^{-1}, he fails to include this in his table of HONO bands because N_2O_3 has absorption in this region. This band, however, seems too intense to be accounted for on the basis of N_2O_3 present. It seems probable that the bands at 1260 and 1298 cm^{-1} are bending frequencies for the two forms of HONO. In the deuterium compound only one band is observed, the two bending frequencies having presumably shifted so as to be nearly identical.

The pair of bands near 800 cm^{-1} assigned by Jones as arising from Fermi resonance between ν_4 and the overtone of an unobserved fundamental are shown by the temperature studies to be due to different molecules. Accordingly, we assign both as N−O stretchings. Since no absorption of HONO was found near 430 cm^{-1}, his assignment of the band at 856 cm^{-1} as $2\nu_5$ is certainly incorrect.

In the 600 cm^{-1} region at least three strongly overlapping bands are observed. The envelopes of the bands at 543.2 and 637.5 cm^{-1} indicate they are type C bands, and their assignment to the torsional oscillations is further supported by their large isotope shift upon deuteration. Another possibility would be to assign them as some odd harmonic of this vibration. Since this alternate assignment would mean that at room temperature a large fraction of the molecules would have this mode excited, one might expect to find excited state transitions. Since no such "hot" bands were observed, the assignment as fundamentals seems more probable. The high intensity of these two bands also suggests that they are not third or fifth harmonics.

The very intense band at 598 cm^{-1}, which shifts to 591.5 cm^{-1} upon deuteration, is with little doubt an O-N-O bending. Although only one band is observed, the asymmetry is such as to suggest another weaker band underneath.

The next task is to divide the absorptions between the cis and trans isomers.

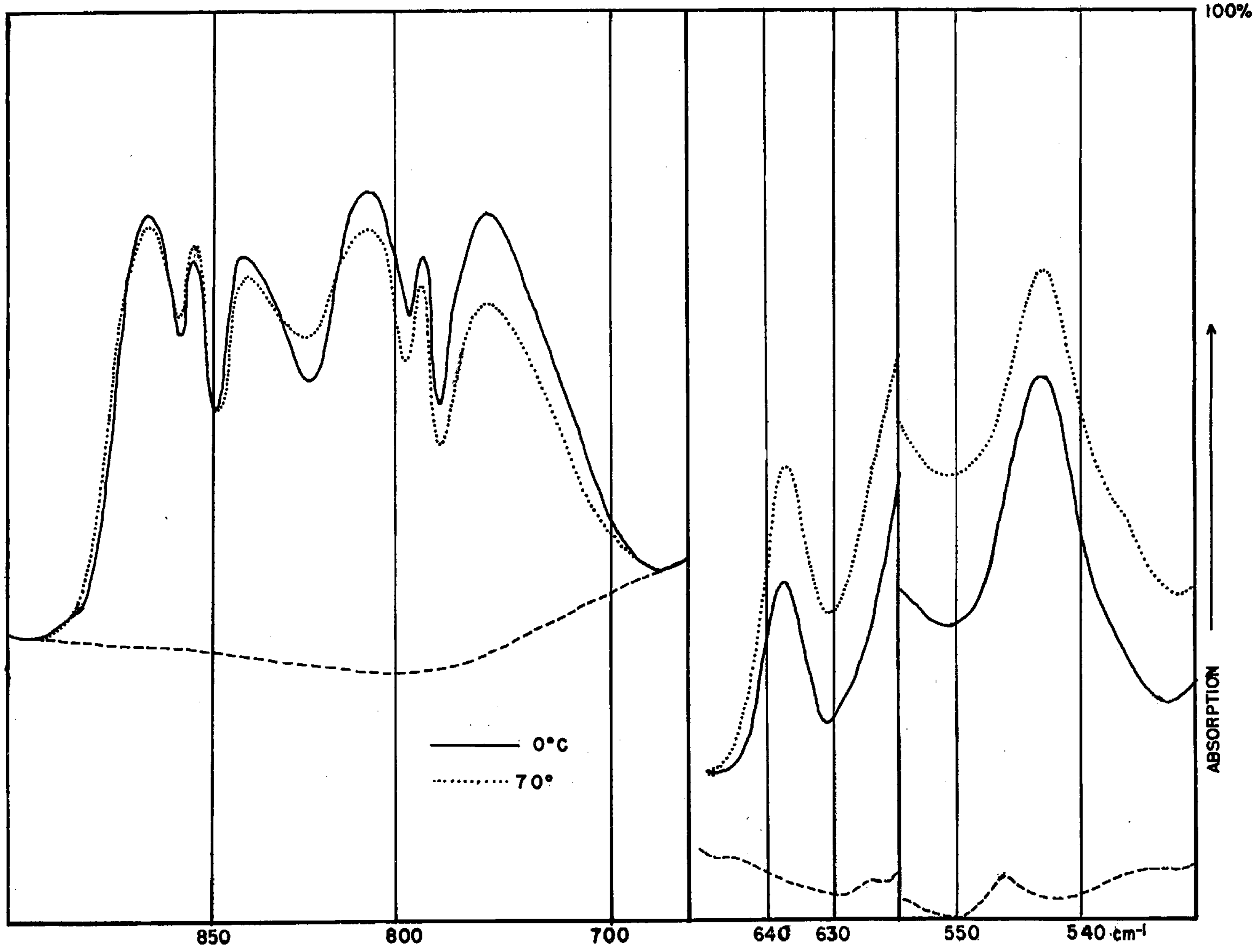
Jones was able to assign only the O-H stretching frequencies to specific isomers. Arguing both from the direction of the transition moment and from the change in large rotational constant upon deuteration, he showed quite conclusively that the band at 3426 cm^{-1} belongs to the cis isomer, leaving 3590 cm^{-1} for trans-HONO. The large rotational constant for cis-HONO was found to be 2.40 cm^{-1}. The type C band at 543.2 cm^{-1} yields a rotational constant of 3.2 cm^{-1}, indicating clearly that is is not a cis absorption. It is assigned to ν_6-trans, leaving 637.5 cm^{-1} for ν_6-cis.

Figure 4 exhibits the central Q-branches of ν_6-cis and ν_6-trans at 0° and 70°. Graphical integration under these maxima, making allowance for overlapping absorptions, shows quite definitely that the ratio of intensities of ν_6-trans to ν_6-cis is lower at 70° than at 0°.

Figure 4.

Left Half: Relative intensities of HONO bands at 856 and 794 cm^{-1} at 0° and 70°.

Right Half: Relative intensities of central Q-maxima of the HONO bands at 543.2 and 637.5 cm^{-1}.


100%
ABSORPTION
850
800
700
640
630
550
540 cm-1
0°C
70°

This establishes that the trans isomer is the more stable form and offers a method of discriminating between the isomeric absorptions. Since the effect is quite small, positive identification can be expected only in favorable cases, where the two bands have roughly the same intensity and are at least fairly well separated. A pair of bands which meets these requirements is the pair of N—O stretchings at 794 and 856 cm^{-1}. Figure 4 shows also that the 856 cm^{-1} band belongs to the isomer of higher energy, which has been identified as cis, leaving 794 cm^{-1} for ν_4-trans.

For the remaining three pairs of fundamentals it was not possible to use the criterion of the temperature effect to separate cis from trans. For ν_5 only one band is observed, while the two ν_3's overlap very considerably and one of the ν_2's is masked with NO_2 absorption. Since the spectra of both HONO and DONO were observed, the Teller-Redlich product rule for the shift of vibrational frequencies upon isotopic substitution (9) can be used to yield a separation of the remaining fundamentals.

Correcting the hydrogen stretching frequencies for their convergence and using the same values of ν_5 for both cis and trans, products were calculated for the various possible combinations of frequencies for ν_2 and ν_3. These are tabulated in Table V along with the products predicted from the product rule. When corrections for anharmonicity are not applied to the observed frequencies, the products observed will usually be smaller than predicted, corresponding to the usual negative convergence constants for the vibrational levels (10). This is the case for the A" vibrations, which products are each about 1% lower than

Table V. Predicted and observed products for various alternative assignments.

		cis	trans
Predicted	A'	1.918	1.889
	A"	1.269	1.317
Observed	A"	1.257 (deviation -0.95%)	1.303 (deviation -1.05%)

Assignment	HONO	DONO	A' Product	Deviation	HONO	DONO	A' Product	Deviation
1)	1640 1260	$1610cm^{-1}$ 1018	1.839	-4.20%	1696 1292	$1690cm^{-1}$ 1018	1.902	0.69%
2)	1640 1292	1610 1018	1.886	-1.70%	1696 1260	1690 1018	1.860	-1.54%
3)	1696 1260	1690 1018	1.816	-5.43%	1640 1292	1610 1018	1.931	2.23%
4)	1696 1292	1690 1018	1.858	-3.91%	1640 1260	1610 1018	1.888	-0.05%

predicted. The A' products which best satisfy this condition are obviously those given by the second alternative assignment in Table V. Accordingly we assign 1696 and 1260 cm^{-1} to ν_2 and ν_3-trans, respectively, and 1640 and 1290 cm^{-1} to corresponding cis vibrations. This assignment is in agreement with the fact that the trans isomer is of lower energy and hence more prevalent; the bands assigned to the trans molecule are in both cases the stronger.

The assignment of overtones and combinations is quite straightforward. Most of these turn out to be bands of the trans isomer, again in agreement with its larger abundance.

STRUCTURE OF HONO

While Jones obtained good values for the large rotational constant, $A-\frac{1}{2}(B+C)$, for both light and heavy cis nitrous acids, the final values of structure parameters he favored were in poor agreement with his rotational constant for DONO. Since the two rotational constants allow one to determine two parameters, Jones' data will be used to calculate the O-N-O angle and the long N-O distance. Not only are these the most difficult parameters to estimate, but they are also the ones in which small changes most influence the small moment of inertia. Accordingly, the others will be estimated and these will be calculated.

Jones estimated the O-H distance in cis nitrous acid to be 0.98 Å by Badger's rule; this value is probably correct to 0.01 Å. By the same method the O-H distance in trans is 0.97 Å. While the H-N-O angle is not easily predicted, it has relatively little influence on the rotational constant; a value of 103° is taken for the cis form. From a comparison of the force constants in N_2O (11) and NO_2 (12) with that calculated by Jones for the nitrogen-oxygen double bond in nitrous acid one concludes that the nitrogen-oxygen distances in these three compounds are quite similar. Since the distances in N_2O and NO_2 are accurately known to be 1.191 Å (13) and 1.188 Å (14) respectively, the distance in nitrous acid is taken as $1.20 \pm .02$ Å.

From the rotational constants and the above estimated parameters one calculates the O-N-O angle to be 114° and the N-O distance 1.46Å. These values are probably correct to within 1° and 0.03 Å respectively.

From the subbands observed in ν_6-trans one can get a rough value of the rotational constant for the trans species. In order to use the combination differences to obtain the rotational constants it is necessary to observe structure in both P and R branches. Since this was not possible, the rotational constant was determined from the average spacing of sub-bands in one branch. From this spacing $A-\frac{1}{2}(B+C)$ for trans is 3.2 ± 0.2 cm^{-1}. For unexplained reasons the corresponding band in DONO was not resolved, so only one parameter can be determined for the trans molecule. Assuming the nitrogen-oxygen distances to be the same as in cis and using a little larger H-O-N angle of 105° because intramolecular hydrogen-bonding is no longer possible, one calculates an O-N-O angle of $118 \pm 2°$.

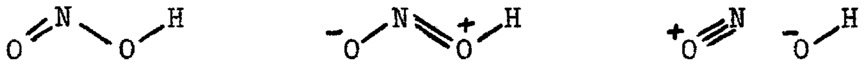
The parameters preferred for cis and trans nitrous acids are collected in Table VI together with the corresponding moments of inertia.

Table VI. Structural parameters and moments of inertia of nitrous acids.

	cis	trans
r_{O-H}	0.98 Å[a]	0.97 Å[a]
$r_{N\ O}$	1.20[a]	1.20[a]
r_{N-O}	1.46[b]	1.46[c]
$\measuredangle_{HON}$	103°	105°
$\measuredangle_{ONO}$	114°[b]	118°[b]
I_A (g-cm^2)	10.13×10^{-40}	7.83×10^{-40}
I_B (g-cm^2)	68.4×10^{-40}	75.2×10^{-40}
I_C (g-cm^2)	78.5×10^{-40}	83.0×10^{-40}

[a] Estimated with assistance of frequency and force constant comparison
[b] Calculated from rotational constants using remaining parameters
[c] Assumed to be same as in the cis form

A striking fact about these sets of parameters is the long N-O distance of 1.46 Å. Since this N-O distance is longer than the 1.43 Å Schomaker and Stevenson (15) give for a single bond, the resonance forms must involve a structure with a weak nitrogen-oxygen bond. A set of resonance structures which fits this condition is



I II III .

A similar explanation was given by Ketelaar and Palmer (16) for the very long N-Cl distance of 1.95 Å found by electron diffraction of nitrosyl chloride. Since the N-O bond length is only slightly greater than that for an ordinary single bond, one might conclude that structures II and III are of approximately equal importance in the electronic structure of nitrous acid.

The contribution of III offers explanations for two observations which at first glance seem surprising. The stability of the trans form relative to cis is explained by a greater tendency of the $(O-H)^-$ dipole to line up with its negative end, ie., the oxygen atom, nearer the positive oxygen atom in the $(O\equiv N)^+$ dipole. If the contribution of III varies with O-N-O angle, the type A structure of the O-N-O bending vibration is explained. Such a variation would result in a shift of charge during this vibration approximately parallel to a line joining the oxygen atoms. Such a shift of charge would yield a transition moment in this direction, approximately parallel to the axis of least inertia, resulting in the observed type A band.

THE BARRIER FOR HINDERED ROTATION

The frequencies of the torsional oscillations coupled with the energy difference of the two isomers allow one to fit a three term potential function to the rotation of the hydrogen about the nitrogen-oxygen single bond. This is carried out in Appendix II resulting in the expression

$$V\ (\text{kcal. mole}^{-1}) \cong 5.96 - 0.745 \cos\theta - 5.70 \cos 2\theta + 0.483 \cos 3\theta,$$

where θ is measured from the trans equilibrium position. This function has a maximum of nearly 12 kcal above the trans configuration at $\theta = 95^\circ$. This suggests that for a first order mechanism for the interconversion of cis and trans nitrous acids the reaction would be nearly complete in the order of a millisecond. Certainly for our temperature studies this equilibrium had been obtained.

It is interesting to note that although the cis minimum is shallower than that of the trans, it has greater curvature, corresponding to the higher cis torsional frequency.

COMPARISON WITH OTHER RESULTS ON NITROUS ACID

Soon after the completion of this work D'Or and Tarte (17) published briefly on a similar investigation of nitrous acid and the alkyl nitrites. Professor Badger contacted Dr. D'Or and received from him a detailed account of their investigation on nitrous acid. The two completely independent investigations yield results in nearly perfect harmony. While D'Or and Tarte had only prism instruments and their spectrometer began to fail near 500 cm^{-1}, from 2 - 18μ only one discrepancy in assignment arises. The location of the weaker H-O-N bending vibration is given by them as ~1370 cm^{-1} while we consider 1292 cm^{-1} more probable. Agreement of other frequencies is within a few wave numbers and often within 1 cm^{-1}. They find several weaker bands throughout the spectrum which they assign to specific combinations and overtones. While some of these are very probably nitrous acid, it seems quite possible that others are contamination bands from reactions of the nitrous acid mixtures with their alkali halide windows. Their careful observations in the 6μ region indicate the presence of bands at 1639 cm^{-1} in HONO and 1620 cm^{-1} in DONO, in good agreement with our values of 1640 and 1610 cm^{-1} calculated from the overtones. Our work beyond 18 μ seems considerably more reliable. Their spectrometer did not show the rotational structure in ν_6-trans of HONO, nor did they locate either of the torsional vibrations in DONO. While the central Q-branch of ν_6-cis of DONO shows in their tracing, they assign it to a P-branch of ν_5-cis. Since our preliminary experiments with KBr windows showed a very strong contamination band in this region, it is remarkable that they were able to do as well as they did.

It is interesting to note that both investigations yielded the same division of bands between cis and trans. This is especially noteworthy since they worked completely by analogy to the alkyl nitrites for the nitrite frequencies and to hydrogen-bonded alcohols for the hydrogen frequencies. Their assignment of nitrite frequencies was made to correspond to that obtained by observation of the temperature effects on methyl and ethyl nitrites, while their hydrogen frequencies were assigned assuming a strong intramolecular hydrogen bond in the cis isomer. In the hydrogen-bonded alcohols the O-H stretching frequencies are lower than normal while the bendings are increased in frequency (18); accordingly, they assign the low stretching and high bending hydrogen frequencies to cis nitrous acid. Our division between cis and trans is identical but from completely different considerations.

B. The Infra-red Spectrum and Structure of the Chloramines and Nitrogen Trichloride

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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.

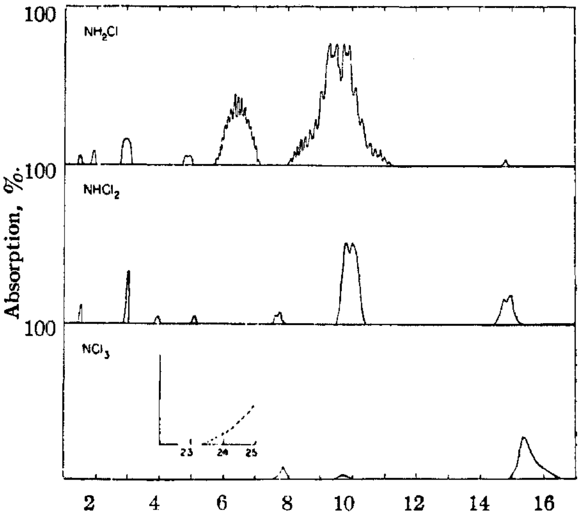

Fig. 1.—Prismatic spectra of NH_2Cl, $NHCl_2$ and NCl_3 reduced to per cent. absorption: path lengths 80 cm.; total pressure, 10 cm. in each case; partial pressures unknown.

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).

(4) R. M. Badger, L. R. Zumwalt and P. A. Giguère, *Rev. Sci. Instruments*, **19**, 861 (1948).

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

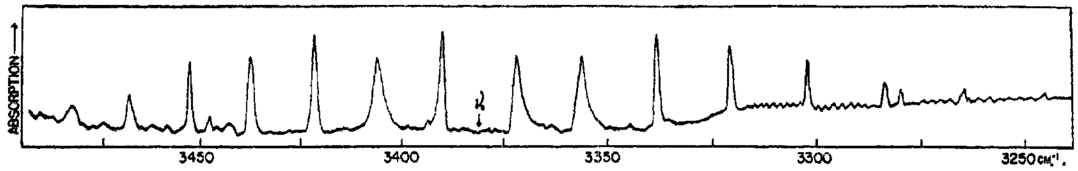

Fig. 2.—ν_5 of NH_2Cl: ν_1 of $NHCl_2$ shows weakly at low frequency end of tracing; path length 80 cm.; total pressure, 10 cm.; maximum absorption is about 45%.

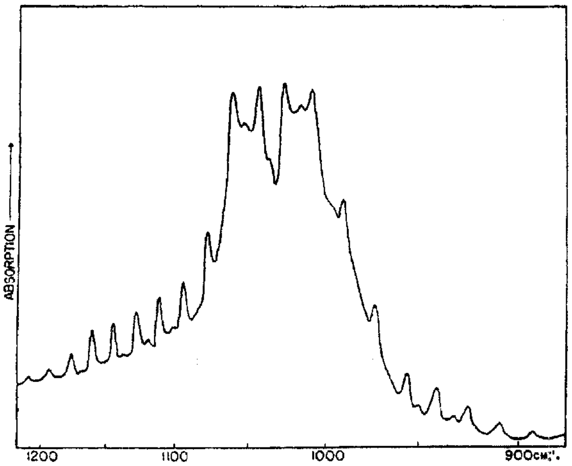

Fig. 3.—ν_3 of NH_2Cl: weaker maxima are probably NH_2Cl^{37}; path length 80 cm.; total pressure, 10 cm.; maximum absorption is about 85%.

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.

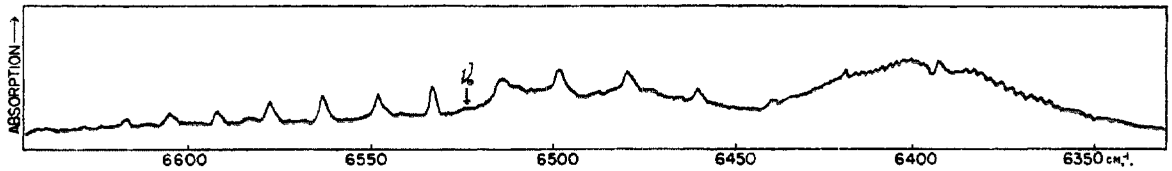

Fig. 4.—$\nu_1 + \nu_5$ of NH_2Cl and $2\nu_1$ of $NHCl_2$: path length 1 meter; total pressure, 10 cm.; maximum absorption is about 25%.

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

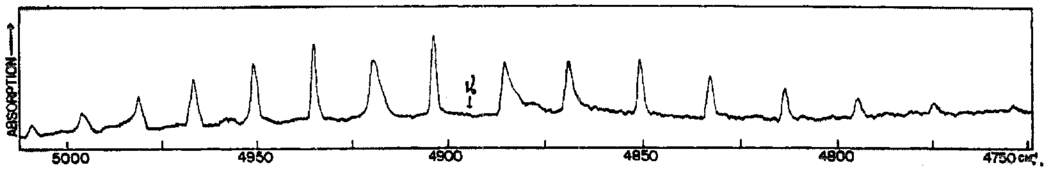

Fig. 5.—$\nu_2 + \nu_5$ of NH_2Cl: path length 1 meter; total pressure, 10 cm.; maximum absorption is about 20%.

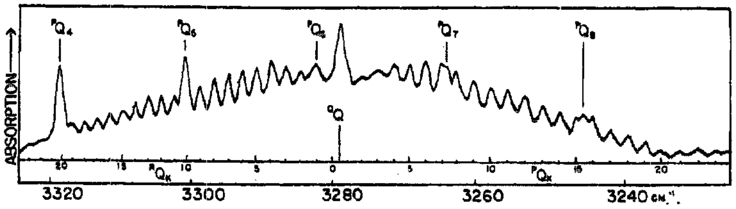

Fig. 6.—ν_1 of $NHCl_2$: maxima numbered on top are part of ν_5 of NH_2Cl; path length 80 cm.; total pressure, 10 cm.; maximum absorption is about 55%.

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.

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.

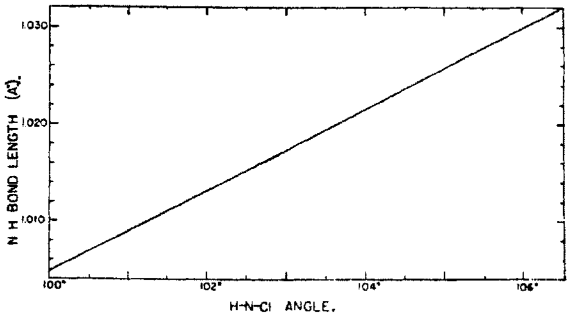

Fig. 7.—r_{N-H} against $<$H–N–Cl consistent with rotational constants for NH_2Cl and NHDCl: r_{N-Cl} = 1.76 Å. and $<$H–N–H = 106°47′.

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.

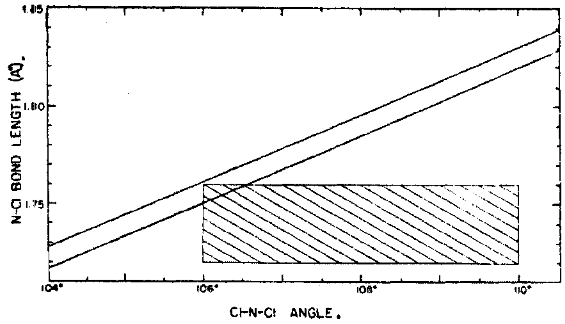

Fig. 8.—r_{N-Cl} against ∠Cl–N–Cl for $NHCl_2$: top curve, r_{N-H} = 1.014 Å., ∠H–N–Cl = 102°; bottom curve, r_{N-H} = 1.014 Å., ∠H–N–Cl = 105°. Shaded area is that allowed by electron diffraction on CH_3NCl_2.

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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[11] Reference 10, p. 295.

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C. The Spectrum of Nitrogen Dioxide in the 1.4-3.4μ Region and the Vibrational and Rotational Constants of the NO_2 Molecule

INTRODUCTION

Considerable interest has centered about the NO_2 molecule. Theoretically it is important as one of the few stable free radicals. It is particularly interesting as possibly the only stable triatomic molecule with an odd electron which is sufficiently light to allow reasonably complete resolution of its vibration-rotation spectrum. In addition, an accurate knowledge of its energy levels is important for developing the thermodynamic functions of NO_2, especially at high temperatures.

The history of NO_2 is extensive and varied. It seems worthwhile to review some of the work bearing on its molecular configuration and the assignment of its fundamental vibrational frequencies.

Aside from the very early work (18), the infra-red spectrum of NO_2 was first investigated by Bailey and Cassie (19) in 1933 in the region out to 18 μ. These investigators observed several bands at room temperature; but when the gas was heated to 100° only two bands remained, 1620 cm^{-1} and 641 cm^{-1}. These two strong absorptions, both appearing as doublets under the rather low dispersion employed, were interpreted as the two infra-red active fundamentals expected for a linear symmetric molecule ($D_{\infty h}$). Accordingly, such a structure was considered by them as proven.

Harris, Benedict and King (20), who had been investigating the electronic band spectrum of NO_2 in the visible and ultra-violet regions, took exception to the interpretation by Bailey and Cassie. These authors argued that the complexity of the rotational structure of discrete ultra-violet bands could not be reconciled with a linear model for NO_2. The structure of the isolated band at 2491 Å in particular required rotations about at least two different axes of inertia, possible only if the molecule is non-linear in both the normal and excited states. They concluded that the angle between the nitrogen-oxygen bonds was greater than 110° but significantly less than 180°. Their observation of bands displaced to longer wave lengths from 2491 Å by amounts 751.1 and 1321.1 cm^{-1} and of the temperature sensitivity of the relative intensities of these displaced absorptions led them to conclude that these were vibrational frequencies of the ground state. They concluded that 751.1 cm^{-1} was the bending ν_2, and 1321 cm^{-1}, the symmetric stretching ν_1. Bailey and Cassie (21), however, objected rather strongly to these conclusions and reasoned on the basis of the number of electrons present for bonding that NO_2 had indeed the linear symmetric structure.

Also during 1933 Schaffert (22) published his results for the spectrum of NO_2 between 2 and 16 μ. By studying the absorption of a NO_2-N_2O_4 equilibrium mixture between 3° and 150° he concluded that NO_2 had absorption bands at 3000, 1628, 1373, and 641 cm^{-1}. By considering 1373, 641, and 1628 cm^{-1} to be the fundamental frequencies ν_1, ν_2, and ν_3, respectively, Schaffert calculated, on the assumption of a valence force field, that the bond angle was about 115°.

In 1934 Harris and King (23) published the results of their investigation of the infra-red spectra of NO_2 and N_2O_4 in the region

1-4 μ. They attributed several bands to NO_2 and assigned them all to specific combinations and overtones of the fundamentals 1321, 648, and 1621 cm^{-1}. They admitted, however, that their interpretation was not unique and other assignments of fundamentals fit their data nearly as well.

Also in 1934 the results of the high dispersion investigation of certain NO_2 bands by Sutherland was published (24). In particular he investigated bands at 1615, 2226, and 2910 cm^{-1} with resolving power he thought sufficient to resolve lines separated by less than one wave number; for the band at 1615 cm^{-1} his spectrometer was claimed capable of resolving 0.5 cm^{-1}. Yet he observed no rotational structure in any of the bands. The envelopes of all three absorptions appeared as doublets, and Sutherland detected no evidence of a central Q-branch, which one might expect in these bands according to their assignment to vibrations antisymmetric with respect to the two fold axis (ie., transition to a B_1 level). He considered this apparent lack of central Q-branch as sufficient reason to suggest that the axis of least inertia of NO_2 was parallel to the two-fold symmetry axis and, accordingly, proposed that the bond angle was less than 58°.

Both Badger and Herzberg in private communications to Sutherland (25) pointed out that the acute angle structure was unlikely. Badger pointed out that the low value accepted for the bending frequency (648 cm^{-1}) was inconsistent with such a structure, while Herzberg showed that the fine structure of the ultra-violet bands required a wide angle. In 1935 Sutherland and Penney (26) concluded from electronic considerations that an angle of 110-120° was more probable than

58°. By assumption of a valence force field and taking $\nu_1 = 1321$ cm^{-1}, $\nu_2 = 648$ cm^{-1}, and $\nu_3 = 1621$ cm^{-1} these authors (26) calculated an angle of 114°.

In 1938 Giauque and Kemp (5) published the results of heat capacity measurements on $NO_2 \rightleftharpoons N_2O_4$. From the third law of thermodynamics and the equilibrium data for the reaction $NO_2 = NO + \frac{1}{2}O_2$ they calculated the entropy of NO_2. Taking the vibrational assignment of Sutherland and Penney, they proceed to calculate a value for the product of the three moments of inertia. Pauling (27) combined this product of moments with a predicted bond length of 1.18 Å to obtain an angle of 133° ± 5°, in fair agreement with his predicted angle of about 140°.

Although an earlier electron diffraction study (28) had failed to establish the parameters, in 1940 Maxwell and Mosley (29) were able to conclude that the angle was about 130°. Further ultra-violet investigations by Harris, King, Benedict, and Pearse also in 1940 (30) suggested that 1319 cm^{-1} was a totally symmetric frequency of the electronic ground state of NO_2 and less certainly that 749 cm^{-1} was another symmetric frequency. While these authors attempted to explain their observations using $\nu_1 = 1373$ cm^{-1}, they were not very successful in doing so. No ultra-violet differences corresponding to a ground state frequency of 648 cm^{-1} were observed.

In the same year by an incomplete rotational analysis of several complex ultra-violet bands Harris and King (31) arrived at moments of inertia from which they calculated a bond angle of 154 ± 4° and a N-O distance of 1.28 ± 0.03 Å. The disagreement of these values with those of previous workers is rather striking, and the partial analysis upon which they were based is by no means convincing. While a bent symmetric model with a fairly wide angle was by now quite generally accepted, the exact parameters remained in doubt.

At this time, while it was quite certain that the strong band at 1615 cm^{-1} was the fundamental ν_3 and the band observed at 648 cm^{-1} by Bailey and Cassie (19) and Schaffert (22) was generally accepted as ν_2, the frequency of the symmetric stretching vibration had not been established. The infra-red investigation of Schaffert suggested 1373 cm^{-1}, while the ultra-violet bands were more easily interpreted on the basis of 1320 cm^{-1}.

A recent reinvestigation of electron diffraction by NO_2 seems to establish the structural parameters to within rather small limits. Claesson, Donohue and Schomaker in 1948 (32) reported an angle of 132 ± 3° and a bond distance of 1.20 ± 0.02 Å.

Wilson in 1948 (33) undertook a reinvestigation of the infra-red spectrum with hopes of establishing the location of ν_1 and of confirming the structure. By employing silver chloride windows, which are not attacked by NO_2, and by comparing the spectrum observed at room temperature with that at 200° he was able to show that several bands previously attributed to NO_2 were spurious and at the same time to find some new weak absorptions of NO_2, which had been overlooked by previous investigators. In particular he observed a weak band whose center he estimated at 1306 cm^{-1}. This band quite certainly is the symmetric stretching frequency. It exhibits coarse rotational structure with spacing about 15 cm^{-1} between successive maxima in agreement with moments of inertia calculated from the electron diffraction parameters. In addition to this, he observed structure of similar spacing extending over the region from about 900 cm^{-1} to the long wave length limit of his spectrometer at about 660 cm^{-1}. He at first attributed this structure to the R-branch of a bending vibration centered at 648 cm^{-1}. This interpretation offered difficulties, however, such as requiring that the band have twice as many lines as would be predicted from the calculated moments of inertia. These difficulties were resolved by Wilson and Badger (34), who took the band center as 755 cm^{-1} in agreement with the differences observed in the ultra-violet spectrum. Subsequent investigations by Wilson (35) employing a potassium bromide prism have shown this assignment to be correct and the strong band reported by earlier observers near 650 cm^{-1} to be spurious.

Wilson's assignment of fundamentals did not adequately explain all the bands which he attributed to overtones and combinations; therefore his assignment had to be considered as tentative.

For convenience the various structures and assignments of fundamentals proposed are collected in Table VII.

Since the suggested spacing of 0.85 cm^{-1} in type A bands seemed to offer a reasonable test of our new grating, it was decided to reinvestigate the spectrum of NO_2 in the region 1.4 – 3.4 μ with the hope of clearing up the vibrational assignment by observing as many combinations and overtones as possible and of refining the structural parameters. This investigation was rewarding in both respects as well as in yielding some interesting and unexpected observations.

Table VII. Various structures and vibrational assignments proposed for NO_2.

Year		Ref. No.	ν_1	ν_2	ν_3	∢ O-N-O
1933	Bailey and Cassie	19, 21	inactive	641	1620	180°
1933	Harris, Benedict and King	20	1321.1	751.1	1620	110°-180°
1933	Schaffert	22	1373	641	1628	115°
1934	Harris and King	23	1321	648	1621	
1934	Sutherland	24	1373	648	1615	$<58°$
1935	Badger, Herzberg (independently)	25	1615	648	1373	$>90°$
1935	Sutherland and Penney	26	1373	648	1615	110°-120°
1939	Pauling	27				~140°, 133 ± 5°
1940	Maxwell and Mosley	28				130°
1940	Harris and King	31	1321	749	1615	154° ± 4°
1948	Claesson, Donohue, & Schomaker	32				132° ± 3°
1948	Wilson	33	1306	648	1615	Consistent with 132°
1949	Wilson and Badger	34	1306	755	1615	Consistent with 132°
1953	This investigation	-	1322.5	750.9$^{(a)}$	1616.0	134°4' ± 15'

(a) From measurements of Wilson and Brown

EXPERIMENTAL

The spectrum of NO_2 was observed with our vacuum grating spectrometer using PbS and PbTe photo-conducting detectors. The grating employed is an original with 7500 lines per inch and a ruled area 5"X6". It is ruled in an aluminum layer deposited on a glass disc 7 3/4" in diameter and 1 1/4" thick and squared to 7"X7". Its blaze is at about 3.5 μ in the first order. In the present investigation resolution of approximately 15,000 was achieved, which was limited by the lack of sensitivity of the detecting system rather than by imperfections in the optics of the instrument. Down to the smallest slit-widths employed (0.04 mm) no deviation from the resolving power calculated from the dispersion of the grating was observed. For the bands of NO_2 the separation of maxima was greatly limited by the breadth of these maxima. Wave length calibration was effected by observing the emission spectrum of sodium vapor (36) as well as the absorption bands of H_2O (37), CO_2 (38) and CH_4 (39). Sodium lines were obtained from a sodium arc lamp of the type used for polarimetry. While lead sulfide cells in general are relatively insensitive to light of wave length less than 1 μ, the intensity of the D-lines in such an arc is sufficient to allow one to use these lines in several orders as well as the doublets near 0.8 μ, 1.1 μ and 2.34 μ. No reference was found to the 2.34 μ doublet, but its frequency was calculated from the well known term values of ^2D (4d) and ^2P (4p). It might be mentioned in passing that the Na line listed (40) in the literature as λ 1.84595 (^2F (3f)-^2D (3d)) has been remeasured as $\lambda_{air} = 1.84662 \mu$ consistent with the new calibration. This allows one to establish the lowest ^2F term in sodium as 34,586.78 ± 0.10 cm^{-1} rather than 34,588.6 cm^{-1} (36).

A large scale plot was made of n $(N-N_0)$ ν vs N, where N is a number read from a Veeder counter and proportional to distance along the sine screw that rotates the grating, N_0 is the reading of the counter at the zero order of the grating, ν is the frequency of the line, and n is the grating order. This plot can be represented as a superposition of a fairly smooth curve and a correction function $\Delta = A(N) \cos (N/6)\pi$ to be added to the smooth curve, where A(N) is a smooth function of the counter number and corresponds to a very nearly constant mechanical amplitude in the grating rotation. The period of 12 counter numbers corresponds to one revolution of the lead screw. The magnitude of this correction is about 0.35 cm^{-1} at 6000 cm^{-1} or 0.10 cm^{-1} at 3600 cm^{-1} in the first order. By adding this correction to the smooth curve, the absolute frequencies are probably determined to about 1 part in 30,000. The distance between lines of the same band reproduces to 0.01 counter numbers or better on different tracings. This corresponds to 0.04 cm^{-1} at 4200 cm^{-1} in the first order. The limiting factor in this case is ordinarily the reproducibility with which one can estimate the line centers.

The value one uses for N_o is a slight function of the slit-width employed. While the mechanical origin of this error has not been established, the magnitude of the correction is known experimentally and seems quite reproducible throughout the spectrum.

Absorption cells 100, 120 and 200 cm in length were used. The 100 and 200 cm cells had pyrex windows fused on, while the 120 cm cell had quartz windows attached with glyptal resin. Provisions were made for heating the cells either by use of a tubular oven or by winding a heating coil directly over the surface of the cell. Since all except two of the NO_2 bands studied could be observed through pyrex windows, interference of any products of the reaction of NO_2 with glyptal was kept to a minimum. Temperatures were measured only roughly by either a thermometer placed under an extra wrapping of asbestos or by a thermocouple included under the heating element. No attempt was made to regulate the temperature accurately, but the heat capacities of the cells exclude the possibility of very large variations during the period of a single run. For most runs the temperature was constant to $\pm 5^{\circ}$.

Two independent sources of NO_2 were used. Some samples were prepared by fractional distillation of liquid N_2O_4 obtained from a commercial cylinder, while others were prepared by reacting purified NO and dry oxygen. Samples of the former were purified as follows: about 30 ml of N_2O_4 from a "lecture bottle" were condensed in a bulb held at 0°; one third of this blue-green liquid was allowed to evaporate; the next third was collected in another bulb; the remaining fraction of the original liquid, now light yellow-brown in color, was discarded; about half of the retained fraction was allowed to evaporate, and the remaining 5 ml of light brown liquid was used directly. In the second method NO was purified by two bulb-to-bulb distillations from dry ice-acetone to liquid nitrogen, the center portion being retained each time. This material was vaporized to fill an evacuated cell to a pressure measured on a mercury manometer and then frozen in a side arm of the cell by liquid nitrogen. An amount of dry oxygen slightly more than sufficient to oxidize all the nitric oxide was quickly let into the cell. Considerable nitric acid appeared in the first preparation. The second contained very considerably less, but in no samples was nitric acid shown to be completely absent. No other presistent impurities were observed.

Pressures of NO_2 in the absorption cells were calculated either from the vapor pressure of N_2O_4 at the temperature of a bulb with which the cell was equilibrated, or from the NO pressure before adding oxygen, together with the equilibrium data for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ (5).

VIBRATIONAL ASSIGNMENT

The frequencies of the centers of all NO_2 bands observed in the present investigation are are listed in Table VIII. Most of the band origins were obtained from analysis of the rotational structure, but in three cases (2905.15 cm^{-1}, 4140 cm^{-1}, and 5974 cm^{-1}) the frequency given is that measured for the sharp edge of a Q-branch. In bands where it was possible to obtain values for the band origin from both resolved structure and a measurement of the Q-branch, the value obtained by the former method has been preferred. In all such cases agreement of the two methods was within 0.4 cm^{-1}.

The observed spectrum is consistent with a molecule of C_{2v} symmetry with the two-fold axis the axis of intermediate inertia. Such a triatomic molecule has vibrational levels that are either symmetric with

Table VIII. Band centers and assignment of NO_2 bands observed.

Frequency (cm^{-1})	Intensity	Band type	Assignment	Figure
2905.15 ±0.3	VS	A	$\nu_1 + \nu_3$	-
[a]3200.2 ±0.3	VW	B	$2\nu_3$	7
4140 ±1.	[c]	A	$2\nu_3 + \nu_2 + \nu_3 - \nu_2$	
[a]4180.10 ±0.1	S	A	$2\nu_1 + \nu_3$	5
[a]4738.87 ±0.1 [b]	M	B	$2\nu_1 + 3\nu_2$	8
[a]4752.50 ±0.1		A	$3\nu_3$	8
[a]5436.80 ±0.1	W	A	$3\nu_1 + \nu_3$	6
5974.9 ±0.2 [b]	W	A	$\nu_1 + 3\nu_3$	9
5985 ±10.		B	$3\nu_1 + 3\nu_2$	9

a from rotational structure

b bracketed bands interacting

c temperature dependent

respect to the two-fold axis (belonging to symmetry class A_1 and giving rise to type B bands in transitions from the ground state) or antisymmetric with respect to this axis, but symmetric with respect to reflection in the plane of the molecule (belonging to symmetry class B_1 and giving type A bands from the ground state). From the rules for multiplication for point group C_{2v}, $A_1 \cdot A_1 = A_1$, $A_1 \cdot B_1 = B_1$, $B_1 \cdot B_1 = A_1$, one sees that all type A bands in absorption from the ground state must involve the asymmetric stretching vibration, ν_3, an odd number of times. All other such absorptions give rise to type B bands.

For the most part the bands are clearly distinguishable as to type, and their assignment to specific vibrational transitions is quite straightforward. The more intense bands are in general of A type, involving odd multiples of ν_3. These include members of the progression $n\nu_1 + \nu_3$ at 2905.15, 4180.1 (Figure 5) and 5436.8 cm^{-1} (Figure 6), as well as $3\nu_3$ at 4752.5 cm^{-1} and $\nu_1 + 3\nu_3$ at 5874.9 cm^{-1} and the "hot" band $2\nu_1 + \nu_2 + \nu_3 - \nu_2$ at 4140 cm^{-1}.

Only one isolated type B structure was observed, a very weak band at 3200.2 cm^{-1} (Figure 7), which is clearly $2\nu_3$.

Two similar regions of anomalous absorption occur near 4750 (Figure 8) and 5980 cm^{-1} (Figure 9), which contain both A and B type structures of comparable intensities. A type B band superimposed upon $3\nu_3$ is ascribed to $2\nu_1 + 3\nu_2$, the only transition of appropriate character lying in this region. The location of the band center at 4738.9 cm^{-1} was suggested by intensity considerations and calculated assuming the essential correctness of a rotational analysis analogous to that for a degenerate vibration of a symmetric rotor. It could be subject to re-

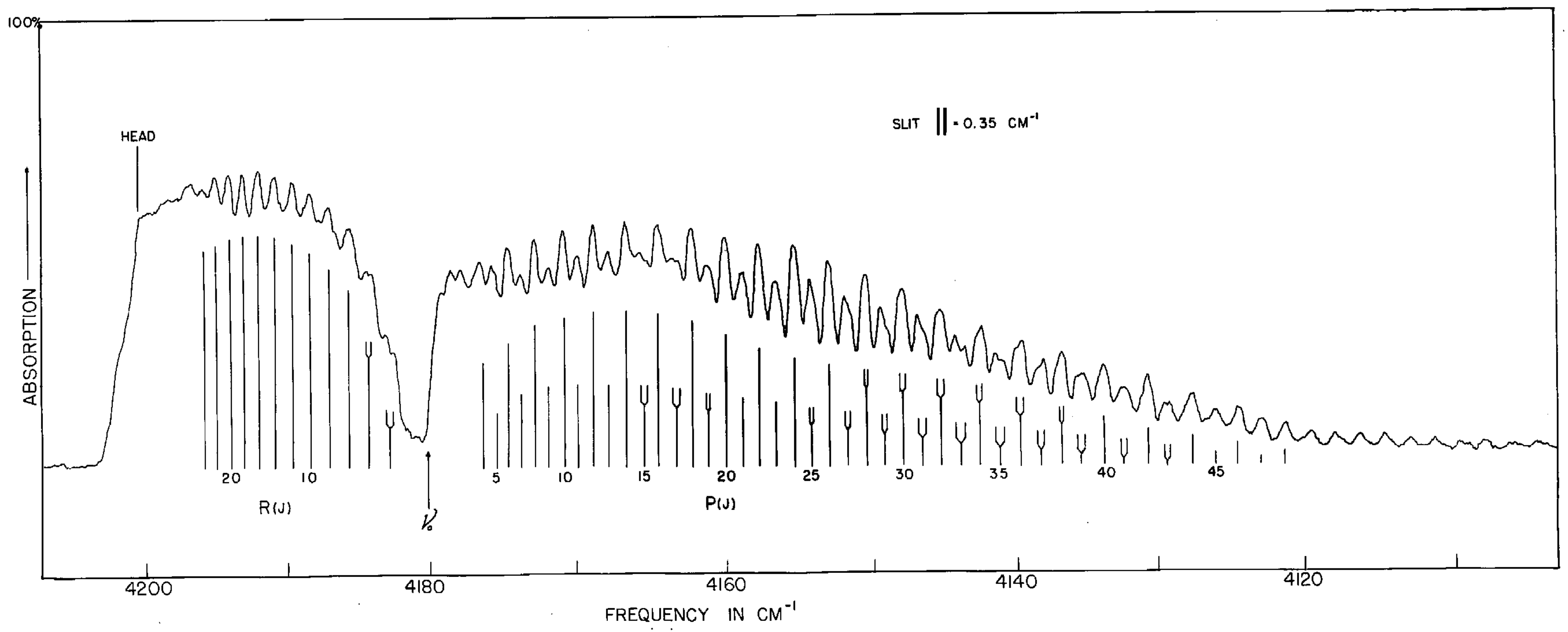


Figure 5. $2\nu_1 + \nu_3$. Cell length 100 cm, P_{NO_2} 33 cm, temperature 60°.

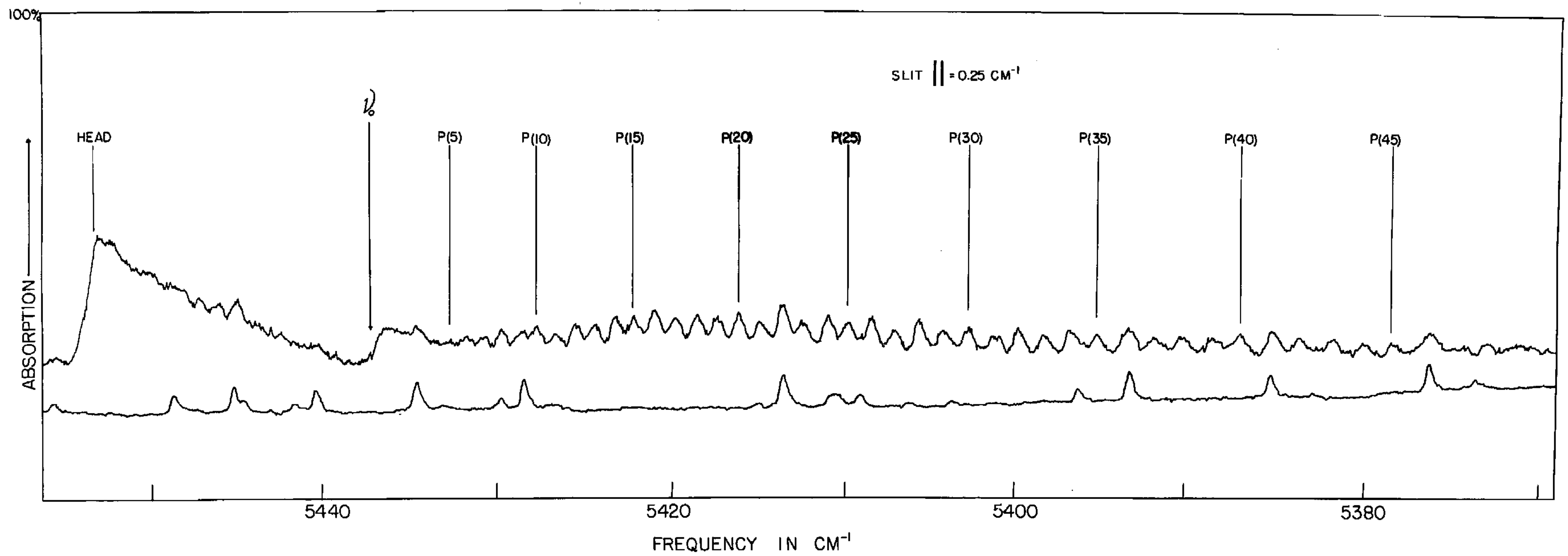
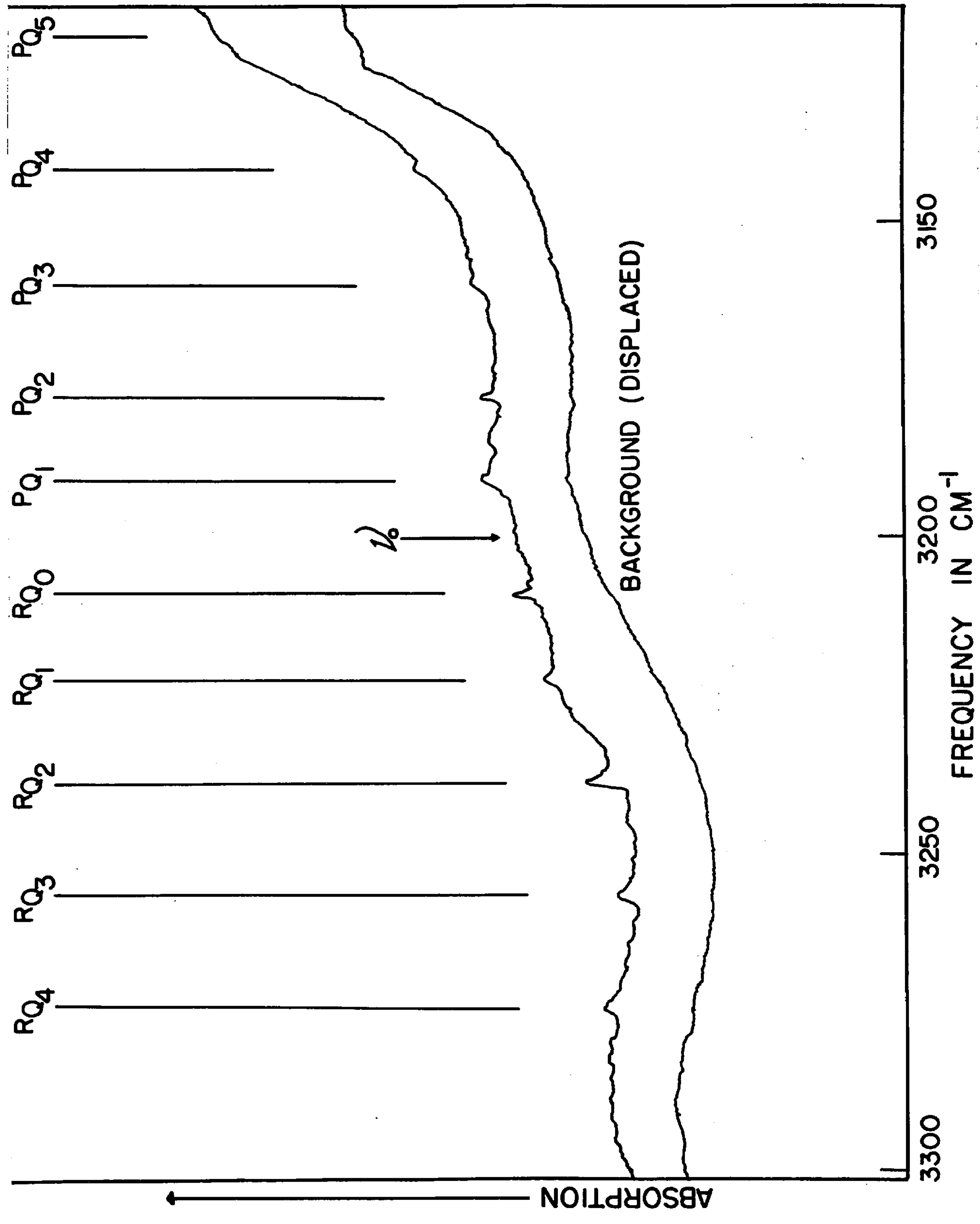


Figure 6. $3\nu_1 + \nu_3$. Cell length 200 cm, P_{NO_2} 112 cm, temperature 165°. The lower curve indicates the positions of overlapping water vapor absorptions.

Figure 7. 2 ν_3. Cell length 120 cm, P_{NO_2} 62 cm, temperature 85°.


$^PQ_5$
$^PQ_4$
$^PQ_3$
$^PQ_2$
$^PQ_1$
ν_0
$^RQ_0$
$^RQ_1$
$^RQ_2$
$^RQ_3$
$^RQ_4$
BACKGROUND (DISPLACED)
3150
3200
3250
3300
FREQUENCY IN CM^{-1}
ABSORPTION

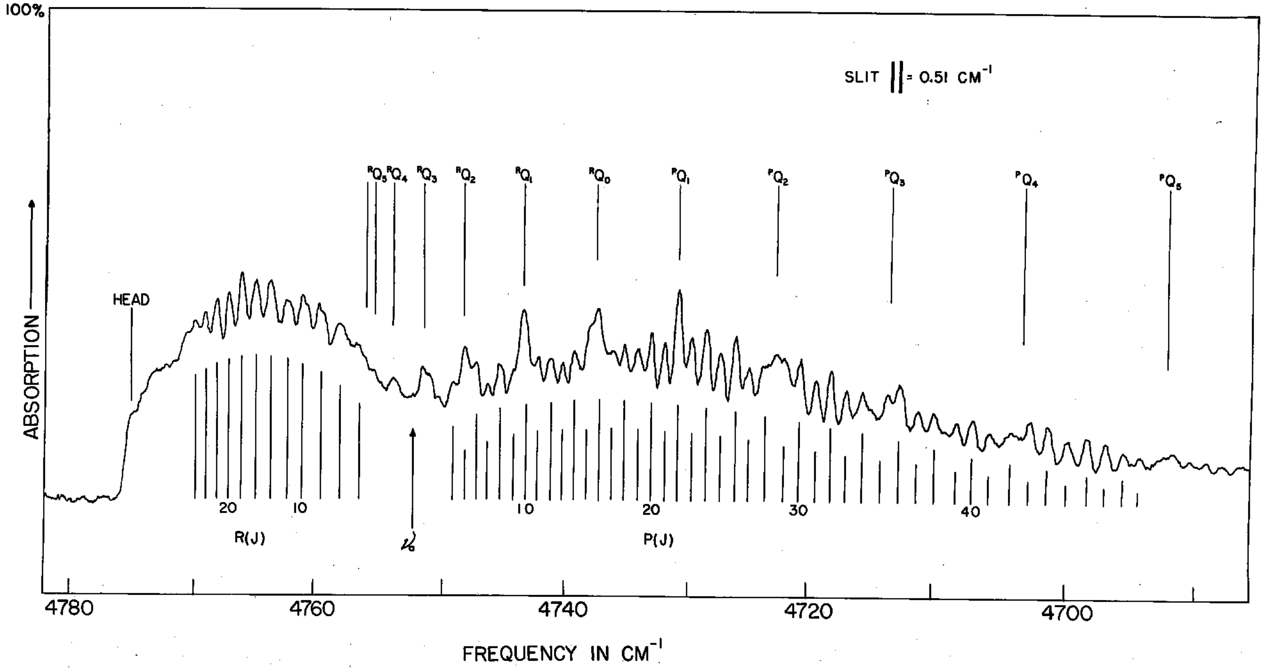


Figure 8. 3 ν_3 and 2 ν_1+3 ν_2. Cell length 100 cm, P_{NO_2} 33 cm, temperature 60°.

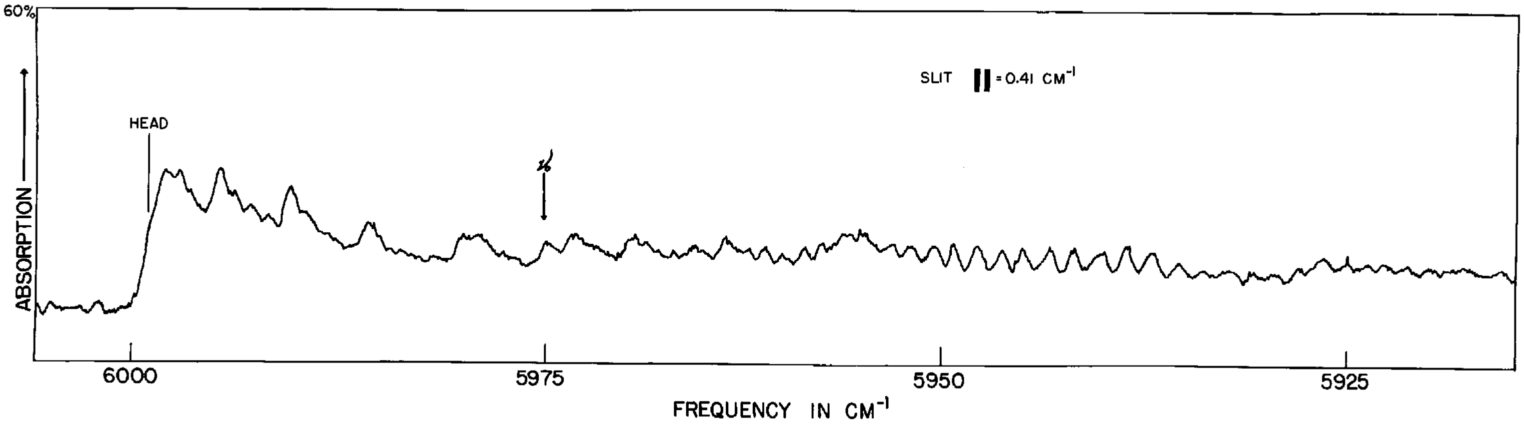


Figure 9. $\nu_1 + 3\nu_3$ and $3\nu_1 + 3\nu_2$. ν_0 refers to $\nu_1 + 3\nu_3$.
Cell length 200 cm, P_{NO_2} 112 cm, temperature 165°.

vision. The structures near 5980 cm^{-1} differ from $3\nu_3$ and $2\nu_1 + 3\nu_2$ by about the frequency of ν_1. They are, accordingly, assigned to $\nu_1 + 3\nu_3$ and $3\nu_1 + 3\nu_2$. Since no other combinations of ν_2 have been observed, it is noteworthy that the two just mentioned have such high intensity. It seems necessary to conclude that they "borrow" intensity from their more active neighbors, although from symmetry considerations this cannot result from a vibrational perturbation.

From the band frequencies and $\nu_2 = 750.9$ cm^{-1} calculated from its observed coarse rotational structure (41), one can calculate all the constants in the general quadratic expression

$$G(v_1,v_2,v_3) = \sum_{i=1}^{3} \omega_i(v_i + \tfrac{1}{2}) + \sum_{i=1}^{j} \sum_{j=1}^{3} x_{ij}(v_i + \tfrac{1}{2})(v_j + \tfrac{1}{2})$$

for the vibrational levels of NO_2. These are tabulated in Table IX.

Table IX. Vibrational constants for NO_2.

$\omega_1 = 1361.4 \pm 1.7$ cm^{-1}	$x_{11} = -7.1 \pm 0.3$ cm^{-1}
$\omega_2 = 770.2 \pm 6.6$	$x_{12} = -16.0 \pm 3.3$
$\omega_3 = 1668.6 \pm 1.7$	$x_{13} = -33.4 \pm 0.1$
$\nu_1 = 1322.5 \pm 0.2$	$x_{22} = -8.1 \pm 3.3$
$\nu_2 = 750.9 \pm 0.4^*$	$x_{23} = -8.2 \pm 3.3$
$\nu_3 = 1616.0 \pm 0.2$	$x_{33} = -15.9 \pm 0.2$

*From data of Wilson and Brown

The constant x_{11} may be determined in three ways. From $2\nu_3$ and $3\nu_3$ one obtains $\nu_3 = 1616.0$ cm^{-1}. The bands $\nu_1 + \nu_3$ and $2\nu_1 + \nu_3$ together with this value yield $x_{11} = -7.1$ cm^{-1}, but with the use of $2\nu_1 + \nu_3$ and $3\nu_1 + \nu_3$ one obtains $x_{11} = -8.4$ cm^{-1}. This discrepancy possibly results from a shift of the level $3\nu_1 + \nu_3$ by about 4 cm^{-1}, through interaction with the slightly higher state $\nu_2 + 3\nu_3$ (calculated at 5491 cm^{-1}), which is not directly observed.

From $\nu_1 + \nu_3$, $\nu_1 + 3\nu_3$, $2\nu_3$ and $3\nu_3$ one calculates $\nu_1 =$ 1322.5 cm^{-1}. While this is not in very good agreement with 1306 cm^{-1} suggested by Wilson, it is in excellent agreement with the value 1321 cm^{-1} obtained from partial analysis of the ultra-violet spectrum (20). Since the band observed by Wilson in the infra-red has type B structure with, accordingly, no well defined center and since it is badly overlapped by a strong N_2O_4 absorption, it seems likely that $\nu_1 = 1322.5$ cm^{-1} is correct. This corresponds to moving the center of Wilson's band approximately the distance between successive Q-branches (15 cm^{-1}).

While the tabulated constants adequately describe the bands observed in this investigation, Wilson has reported absorptions at 1910 cm^{-1} and 3545 cm^{-1} which do not seem compatible. While our high dispersion tracings do indeed reveal a band measured as 3547 cm^{-1}, this band seems to be spurious. Upon heating the gas from room temperature to 100° all bands of NO_2 increase in strength, while this band remains unchanged in intensity. A drop of 70% HNO_3 introduced into an absorption cell yielded the 3547 cm^{-1} absorption strongly, but bands of NO_2, in particular the strong band at 4180 cm^{-1}, were absent. We believe the 3547 cm^{-1} band is the O-H stretching fundamental of HNO_3.

The 1910 cm^{-1} absorption caused Wilson considerable difficulty. He was finally obliged to assign it to the combination $\nu_2 + \nu_3$ and postulate a very large interaction constant. A comparison of his tracings with tracings of NO taken on the same instrument shows that the 1910 cm^{-1} absorption corresponds in position and contour to the R-branch of the NO fundamental centered at 1875 cm^{-1}. Indeed a careful examination indicates that the P-branch is also present in his tracings, but overlapped by a very strong N_2O_4 absorption. From the equilibrium data of Bodenstein and Lindner (42) one calculates that at 200° and total pressure 340 mm the partial pressure of NO from decomposition of NO_2 is 11 mm of Hg. In the 100 cm absorption cell employed by Wilson this pressure of NO is ample to account for the 1910 cm^{-1} absorption.

Except for a weak, diffuse absorption around 800-850 cm^{-1} also observed by Wilson and which might very well be HNO_3, the vibrational constants in Table IX adequately account for all known infra-red bands of NO_2.

ROTATIONAL STRUCTURE

All bands observed in this investigation had rotational structure at least partially resolved (Figures 5 - 9). Their structure clearly exhibits the fact that NO_2 is very nearly a symmetrical rotor, both by the absence of any clearly defined center in the B type bands, and in the simple PQR structure of the A type bands. All analyses of rotational structure have been carried out in the (very good) symmetric top approximation. The measured position of maxima in the type A and B bands are listed in Tables X and XI, respectively.

Table X. Positions of maxima in type A bands.

Band	$2\nu_1 + \nu_2$		$3\nu_1 + \nu_3$	$3\nu_3$	
Q-Branch	4179.8		5436.9	- - -	
Head	4202.3		5454.2	4776.9	
J	P(J)	R(J)	P(J)	P(J)	R(J)
4		4184.30*		4749.07	
5	4175.71				
6	4.57	5.60	5432.02	7.20	4758.07
7	3.72		0.73	6.29	
8	2.78	7.14	5429.73	5.20	9.60
9	1.84		8.55		
10	0.81	8.48	7.66		4760.91
11	4169.88		6.66	2.18	
12	8.80	9.69	5.52	1.24	2.14
13	7.87		4.37	0.25	
14	6.69	4190.96	3.29	4739.30	3.60
15	5.47*		2.29	8.10	
16	4.49	2.16	1.07		4.81
17	3.35*		5419.85	6.24	
18	2.27	3.15	8.63	5.16	5.90
19	1.09*		7.47	4.11	
20	0.03	4.16	6.26	2.95	6.90
21	4158.85		5.07	1.85	
22	7.71	5.25	3.70	0.75	7.93
23	6.62		2.59	4729.73	
24	5.31	6.05	1.02	8.45	8.86
25	4.06*		5409.86	7.19	
26	2.87		8.43	5.98	9.74
27	1.58*		7.10	4.91	
28	0.44*		5.68	3.53	
29	4149.10*		4.24	1.94	
30	7.91*		2.77	0.72	
31	6.56*		1.25	4719.39	
32	5.18*		5399.84	8.15	
33	3.86*		8.30	6.86	
34	2.56*		6.76	5.66	
35	1.12*		5.24	3.73	

(continued)

Table X. - continued

J	P(J)	R(J)	P(J)	P(J)	R(J)
36	4139.77*		3.53		
37	8.31*		2.02	1.17	
38	6.98*		0.49	4709.89	
39	5.48*		5388.73	8.15	
40	4.09		7.23	6.84	
41	2.61*		5.41	5.42	
42	0.93		3.92	3.72	
43	4129.72		1.97		
44	8.11		0.29	0.94	
45	6.52		5378.65	4699.48	
46	5.10		6.52	7.97	
47	3.59		4.89	6.48	
48	2.01		3.31	5.19	
49	0.40			3.80	
50	4118.79			2.38	

* Center of gravity of a doublet

Table XI. Positions of maxima in type B bands.

Band	$3\nu_3$	$2\nu_1 + 3\nu_2$		$3\nu_3$	$2\nu_1 + 3\nu_2$
$^RQ_0$	3209.0	4737.77	$^PQ_1$	3191.0	4730.75
1	22.6	43.54	2	78.0	22.63
2	38.7	48.24	3	60.5	13.04
3	56.8	51.65	4	43.6	02.72
4	74.7	54.40	5	28.1	4691.55
5	87.4	55.45	6		79.52
6		56.50	7		66.34
			8		52.40

The Type A Bands: $\nu_1 + \nu_3$(2905.1 cm^{-1}), 2 $\nu_1 + \nu_3$(4180.1 cm^{-1}), 2 $\nu_1 + \nu_2 + \nu_3 - \nu_2$(4140 cm^{-1}), and 3 $\nu_1 + \nu_3$(5436.8 cm^{-1})

The three isolated type A bands of the progression n $\nu_1 + \nu_3$ exhibit an increasingly strong convergence of the rotational structure toward R-branch heads. Even at room temperature the head of 3 $\nu_1 + \nu_3$ (5436.8 cm^{-1}) is sharp and well defined, while at temperatures in excess of 70° the head of 2 $\nu_1 + \nu_3$ (4180.1 cm^{-1}) is quite prominent. Only in 2 $\nu_1 + \nu_3$ was rotational structure resolved in both P and R branches. The intense band at 2905.1 cm^{-1} was observed with the lead telluride cell, the relative insensitivity of which necessitated a rather wide slit. The weak band at 5436.8 cm^{-1} required the use of high pressures which was attended by pressure broadening of the lines. The last mentioned band was overlaid with the 1.9 μ water band, which, although kept to a minimum, caused some intensity anomalies. These are indicated in Figure 6 which shows a water spectrum for comparison.

The "hot" band 2 $\nu_1 + \nu_2 + \nu_3 - \nu_2$ (4140 cm^{-1}) appears under the P-branch of 2 $\nu_1 + \nu_3$ at elevated temperatures. The stronger overlapping absorption from the ground state precluded a rotational analysis, but temperature dependent intensity anomalies in the P-branch of the ground state absorption allow one to locate the head and Q-branch of the "hot" band to within the spacing of successive maxima ($\sim$1 cm^{-1}).

All the above bands showed a pronounced alternation of intensity in the P-branch. In $\nu_1 + \nu_3$ only the alternate stronger maxima were resolved. Apparently this was true also of the R-branch of $2\nu_1+\nu_3$ where it is possible that no structure would have been resolved in the absence of the intensity alternation. In the latter band many of the P-branch lines appear as doublets. The splitting is apparently always greater for the weaker maxima (J odd) and shows a peculiar dependence on J. It exhibits two maxima of about 0.4 and 0.6 cm^{-1} respectively at $J=17$ and $J=33$, and a minimum at $J=23$, where it is not detectable. While a splitting may be expected both from the spin doubling and the slight asymmetry of the rotor, we have no explanation for the dependence on J unless this results from a weak perturbation by a neighboring level, such as $\nu_1+2\nu_2+\nu_3$ (calculated at 4342 cm^{-1}). A similar splitting was not observed in the other A type bands, but could easily have escaped detection owing to the less favorable conditions of observation mentioned above.

An intensity alternation is to be expected in type A bands because $K=0$ is allowed only for alternate J values, since the O^{16} nuclei have no spin. The magnitude of this alternation can be predicted by use of the symmetric rotor expression for the line intensities in an absorption band.

The intensity of a given transition for a symmetric top in absorption is given by the relation (43)

$$I(J,K)=C\cdot A_{KJ}\cdot\nu\cdot g_{KJ}\cdot e^{-F(K,J)\frac{hc}{kT}},$$

where C is a constant depending only on the particular vibrational (and electronic) transition, where A_{KJ} is proportional to the square of the transition moment summed over all orientations of J, where ν

is the frequency of the transition, and where g_{KJ} and $F(K,J)$ are the statistical weight and term value of the lower state. Taking A_{KJ} for the P-branch of a parallel band and summing the various lines which contribute to a particular $P(J)$ maximum, one gets

$$I(J)_P = C \sum_{\substack{K=0,\ J \text{ even} \\ K=1,\ J \text{ odd}}}^{J} \nu \frac{J^2 - K^2}{j(2J+1)} \cdot g_{KJ} \cdot e^{-F(K,J)\frac{hc}{kT}} \quad .$$

The degeneracy g_{KJ} is $(2J+1)$, again because of the O^{16} nuclei. One calculates that at 25° the ratio of strong maxima to weak near $P(20)$ should be 1.25/1, while at 200° it should be 1.18/1. The observed intensity alternation is possibly somewhat larger than the predicted value and is estimated to lie between 1.3/1 and 1.5/1. It shows a very small, but probably real, decrease with temperature.

At this point it should be mentioned that the resolution of 0.5 cm^{-1} claimed by Sutherland (24) in his observations on ν_3 was almost certainly overestimated since the intensity alternation permits structure to be observed with resolution of only 1.5 cm^{-1}.

The Type B Band, 2 ν_3 (3200.2 cm^{-1})

For a linear symmetric molecule 2 ν_3 would be forbidden in the infra-red. Since NO_2 is slightly bent, this frequency becomes weakly active. While it has been reported by other investigators (44), it is somewhat doubtful that it has previously been observed. Its low intensity and wide spacing make its observation improbable under low resolution.

The band (Figure 7) appears as several weak maxima separated by about 15 cm^{-1}. Its spacing is in agreement with Wilson's observations on ν_1 and ν_2 (32). However, combinations made from the observed Q-branches do not correspond to those from ν_2, although they extrapolate to the same value at $K = 0$. For some unexplained reason the trend in rotational constant with K appears to be opposite in sign from that found for ν_2.

The Complex Structures at 4750 cm^{-1} and 5980 cm^{-1}

Two anomalous regions occur where type A bands are apparently overlaid by type B structure, which shows peculiarities both in regard to intensity, mentioned above, and spacing. In the 5980 cm^{-1} region (Figure 9) the spacing of the B component is irregular and was not analyzed successfully. The A type structure in this region is easily picked out over a region in the P-branch and allows one to locate the Q-branch, which, fortunately, is less diffuse than in some other type A bands. This Q-branch was measured as the band center for the type A structure.

The region near 4750 cm^{-1} (Figure 8) exhibits considerably more regularity. The type A structure seems quite normal, while the B structure shows a regular convergence toward a head. However, if the center of the B structure is located near the maximum of intensity, the observed spacing is only half as large as is found in isolated type B bands.

It seems clear that there is an interaction between neighboring upper levels which give rise to the two types of structures. This cannot be a simple vibrational perturbation since the upper levels belong to different symmetry species and does not appear to be an ordinary Coriolis interaction. A Coriolis interaction between the levels $3\nu_3$ and $2\nu_1+3\nu_2$ would be exceedingly weak according to the rule advanced by Wilson (45), and its effect on the energy should introduce only a term in K^2 into the upper state rotational term values (46). Such an additional term can be combined with the term in K^2 already present and should effect the band structure in a manner completely analogous to changing the upper state rotational constant. This alters the convergence of the lines in an absorption, but has no effect on the average spacing.

An explanation whereby the observed lines are all ^{R}Q maxima with rather high K values, where the spacing has been reduced by convergence, can be ruled out. As the temperature is increased, the wings of the band extend farther in both directions, indicating that both extremes represent relatively high rotational excitation.

The band can be formally accounted for if one assumes that rotational levels of the upper state are split according to an expression of the form applicable to degenerate vibrations of a true symmetric top, namely

$$F(J,K) = J(J+1)\,B' + K^2\,(A'-B') \mp 2\zeta KA'$$

and that the transition rules are the same as for this case (47). In this case sub-bands in the P and R-branches no longer have common upper states; therefore one cannot make the usual combinations. One can, however, make the combinations

$$\begin{aligned} {}^{R}Q_{K-1} - {}^{P}Q_{K+1} &= 4\,(A'' - A'\zeta - B'')\,K \\ {}^{R}Q_{K} - {}^{P}Q_{K} &= 4\,(A' - A'\zeta - B')\,K \quad . \end{aligned}$$

By eliminating A' between these two relations,

$$\zeta = \frac{{}^{P}Q_{K+1} - {}^{R}Q_{K-1} + (A''-B'')\,4K}{{}^{R}Q_{K} + {}^{P}Q_{K+1} - {}^{P}Q_{K} - {}^{R}Q_{K-1} + (A''-B'')\,4K + 4KB'} \quad .$$

Using $B' = 0.418$ cm^{-1} and $(A''-B'')$ from ν_2, one calculates values for ζ ranging from -0.514 at $K = 1$ to -0.508 at $K = 5$. The nearness of these values to $-\frac{1}{2}$ appears suggestive in view of the unpaired electron, but no quantitative explanation was forthcoming. The band center is calculated assuming the essential correctness of this assignment.

Rotational Constants and Structural Parameters of NO_2

The rotational constants in Table XII were obtained in the usual manner from combination differences plotted against K^2 or $J(J+1)$. The ground state rotational constants are $\tilde{B} = 0.429 \pm 0.002$ cm^{-1} from both $2\nu_1 + \nu_3$ and $3\nu_3$ and $A-\tilde{B} = 7.62 \pm 0.05$ cm^{-1} from ν_2 as measured by Brown and Wilson (41). The structural parameters consist-

Table XII. Rotational constants of NO_2

Level	$\tilde{B}$	$A-\tilde{B}$	D_J (X 10^5)	D_K (X 10^3)
ground	0.429 ± 0.002	7.62 ± 0.05	1.0 ± 0.2	5.8 ± 1.2
ν_2	- - -	7.92 ± 0.05	- - -	5.4 ± 1.2
$2\nu_1 + \nu_3$	0.422 ± 0.002	- - -	1.0 ± 0.2	- - -
$3\nu_3$	0.422 ± 0.002	- - -	1.0 ± 0.2	- - -
$3\nu_1 + \nu_3$	0.419 ± 0.003	- - -	- - -	- - -

ent with these rotational constants are $r_{N-O} = 1.188 \pm 0.004$ Å and $\measuredangle$ O-N-O $= 134^\circ 4' \pm 15'$. These are compatible with the electron diffraction data (32) which yield $r_{N-O} = 1.20 \pm 0.02$ Å and $\measuredangle$O-N-O$= 132 \pm 3^\circ$.

SECTION II.

Some Observations Concerning the Photochemical Decomposition of Nitric Oxide

INTRODUCTION

The heat of dissociation of nitrogen is still a subject of considerable controversy. While spectroscopic studies have established it to be either 9.76 or 7.37 electron volts (48), it has not yet been possible to make a clear-cut decision between the two values. Recently several investigators have favored the higher value (49), but extensive studies by electron bombardment point strongly toward 7.37 ev. (50). It was hoped that a study of the photochemical decomposition of NO might aid in settling this controversy.

Thermochemical studies (51) yield for the decomposition of NO to N_2 and O_2

$$2NO = N_2 + O_2 + 1.87 \text{ ev.}$$

Since the heat of dissociation of O_2 is known as 5.08 ev (52), from the two possible values for N_2 the heat of dissociation of NO is either 5.29 or 6.49 ev. If one can distinguish between these values for NO, the corresponding value for N_2 is proved.

Flory and Johnston (53) investigated the photodecomposition of NO at low pressures and found that the lowest frequency line effective in decomposing the gas was a weak line from their mercury arc at 1832 Å, presumably by absorption in the 1,0 band of the δ-system ($C^2\Sigma - X^2\Pi$). Since 1832 Å (6.76 ev) has ample energy to dissociate NO for either value of the dissociation energy, the experiments did not argue strongly for one or the other.

The γ-band system ($A^2\Sigma - X^2\Pi$) in NO shows a particularly marked pressure broadening (54)(55). Wulf (56) explained this broadening as a pressure induced predissociation in the $A^2\Sigma$ level. The first three vibrational levels in this electronic state, all strongly perturbed, are at 5.49, 5.77 and 6.04 ev; so if such an explanation is correct, the heat of dissociation of NO and hence of N_2 must have the lower value. In an attempt to test this hypothesis Gaydon (57) irradiated NO at atmospheric pressure with the light from an iron arc and found no evidence of decomposition after "long exposures".

The emission of an iron arc in the region of the γ-bands is, however, very weak (Figure 10), and it was felt worthwhile to repeat the experiment using a more intense source.

EXPERIMENTAL

Condensed sparks between metallic electrodes in air were used as light sources. The electrical circuit consisted of a 1 KVA, 15,000 volt transformer and a condenser of 0.001 or 0.004 μf in parallel with a spark gap of about 4 mm. When the larger condenser was employed, the tendency of the circuit to arc was substantially decreased by inserting a small gap between steel balls in series with the other spark gap. With the smaller condenser, the quenching effect of the steel spark gap was insufficient. Accordingly, it was removed and instead a strong stream of air was directed on the spark to blow out any arc that might start. Electrodes were originally cast from Zn, but in order to eliminate light of high frequency, later experiments employed Cd electrodes with the light filtered through a rocksalt plate.

Nitric oxide was taken from a commercial cylinder and purified by repeated fractional distillations. Commercial "high-purity" nitrogen was freed of most residual oxygen and water vapor as follows: a glass bulb with a large diameter side arm was filled to a pressure of a few cm of Hg with NO; tank nitrogen was added to atmospheric pressure and the gases were allowed to equilibrate overnight; the NO_2 formed as well as any residual NO and H_2O was then frozen out in liquid nitrogen. This N_2 in the bulb was then used directly. It was found to have a small quantity of oxygen remaining, but the amount was not sufficient to interfere with the results of the experiments.

An absorption cell 25 cm in length and fitted with quartz windows attached with glyptal resin was used throughout. After each filling the NO was frozen in a side arm while the tube was sealed off with a flame. It was kept frozen until the seal cooled to decrease the possibility of decomposition on the hot surface.

In order to minimize the irradiation times by making efficient use of the available light the cell was located with one end a few centimeters from the spark. Accordingly, the light was highly divergent and the front end of the tube received considerably more than did the distant end. Because N_2O_3 absorbs light in the region of the γ-bands, during most runs a side arm on the absorption cell was held at dry ice temperature to trap any N_2O_3 formed by decomposition of NO. While this precaution was usually observed, the amount of N_2O_3 present when not frozen out was found to be insufficient to decrease significantly the rate of decomposition.

Photographs were taken on a small Hilger quartz spectrograph. This instrument has excellent quartz and allows one to photograph readily lines as low as 1830 Å. In several experiments this spectrograph was placed at the opposite end of the absorption cell from the spark and exposures taken at appropriate intervals. Kodak Metallographic and M Plates were used after ultraviolet sensitization by mineral oil dissolved in acetone. This oil was washed off with acetone before developing.

Decomposition was detected by observing the continuous absorption of N_2O_3 in the ultra-violet (58). The background of continuum and weak lines in the light emitted by the spark was used in photographing this very strong absorption, which offers a convenient method of observing small amounts of decomposition at high NO pressures. Quantitative comparisons of amounts of decomposition were made by observing this N_2O_3 absorption with a Beckman DU Spectrophotometer. A special compartment suitable for the 25 cm cell was constructed and the optical density of the cell at various wavelengths between 2100 and 2500 Å was observed relative to an air path.

RESULTS AND DISCUSSION

In Figure 10 exposure (a) shows the emission of an iron arc, while (b) shows a cadmium spark. The exposures were made under similar conditions; the sources were the same distance from the spectrograph slit and the light was taken unfocused from the divergent beam. It is readily apparent that the Cd spark has considerably more intensity in the region below 2500 Å.

Exposure (c) is again the cadmium spark source, but this time the

Figure 10. All exposures were 100 seconds with the same spectrograph settings and source location. The light was taken unfocused from the divergent cone.

a) Iron arc

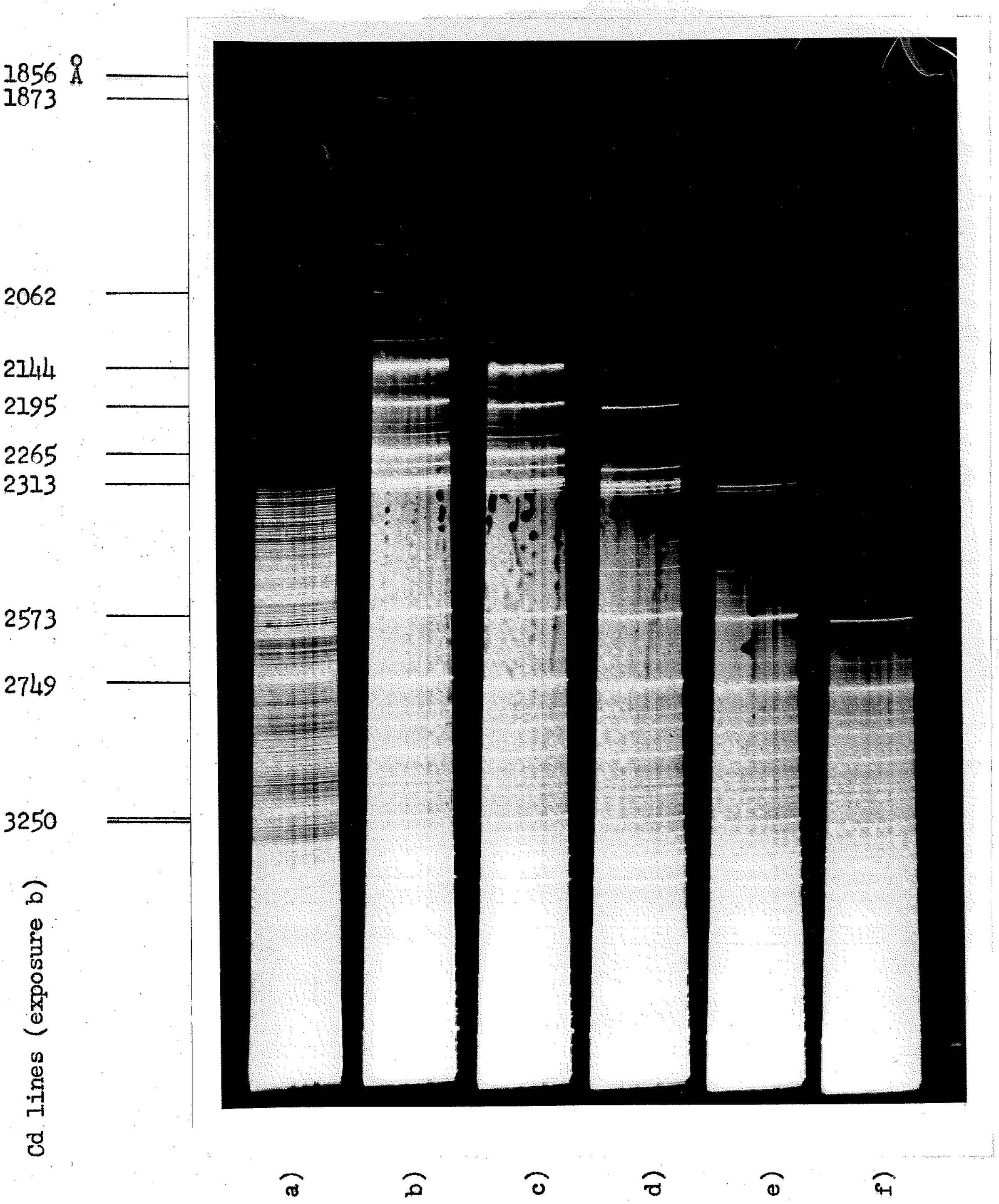
b) Cadmium spark

c) Cadmium spark filtered through 5.7 mm of NaCl

d) Source as in (c) through 25 cm absorption cell filled with NO to 80 cm of Hg.

e) Through absorption cell after 15 minutes of irradiation.

f) Through absorption cell after 1 hour of irradiation.


1856 Å
1873
2062
2144
2195
2265
2313
2573
2749
3250
Cd lines (exposure b)
a)
b)
c)
d)
e)
f)

light has been filtered through a NaCl plate 5.7 mm thick. Comparing with exposure (b), it is apparent that light of $\lambda < 2050$ Å has been effectively filtered out.

Exposure (d) shows the source as in (c)(cadmium spark filtered through NaCl) as viewed through the absorption cell filled with NO to a pressure of 80 cm of Hg. The heads of the 1,0 (2155 Å) and especially the 0,0 (2269 Å) γ-bands are visible. The weak continuous absorption evident in the region of these bands is the N_2O_3 continuum, probably from the amount of N_2O_3 produced during the 100 second exposure. The very strong Cd lines at 2144 and 2265 Å are completely absorbed by the 1,0 and 0,0 bands, respectively. By comparing exposures (a), (c), and (d) one observes the large ratio of cadmium spark radiation to iron arc radiation that is available for absorption by the γ-bands. It is apparent that the spark offers a considerably better source for observing any photolysis of NO by absorption in these bands than does the iron arc as used by Gaydon (57).

Exposures (e) and (f) show the absorption of the same sample of NO as in exposure (d) after 15 minutes and 1 hour of irradiation, respectively, by the filtered light from the cadmium spark. The increase in the strength of the N_2O_3 continuum is readily apparent. In exposure (f) the continuum extends well beyond the Cd line at 2573 Å.

That this decomposition was a photo effect and not caused by either an induced electrical discharge or a small air leak was shown on other samples. To argue against the former, which a priori is very unlikely because of the high NO pressures, a glass disc was fitted over the quartz window on a freshly prepared sample. After four hours of irradiation in the usual manner the glass was removed and an exposure through the spectrograph compared with one taken before the glass window was installed. No change in N_2O_3 absorption was detected. Irradiation of 45 minutes through the quartz window with other conditions the same was then shown to give considerable decomposition.

The possibility of air leaking into the cell and causing apparent decomposition was ruled out by two arguments. First, a freshly prepared sample showed no changes after standing for 7 days, but exhibited decomposition after a brief exposure to the spark at the end of this period. Secondly, decomposition was observed in a cell filled to greater than atmospheric pressure.

While the early experiments with a zinc spark and unfiltered cadmium spark did not rule out the possibility of the decomposition being caused by weak lines of wave length shorter than 1910 Å (6.49 ev), the decomposition by filtered cadmium light showed quite conclusively that the light of $\lambda > 2050$ Å (energy < 6.05 ev) caused decomposition.

A comparison was made of the relative rates of decomposition of a cell filled to 15 cm pressure with pure NO and the cell filled to 15 cm with NO and pressurized with N_2 to 60 cm total. An analysis of the data obtained shows the addition of the N_2 decreased the rate by 15±7%. While the decrease represents an average of five values, all between 0% and 21%, and seems to be statistically significant, the comparison was carried out on only one pair of samples. Since in view of the results by Lambrey (55), which indicate that N_2 is nearly as efficient as NO in broadening the bands, it is difficult to explain this decrease, it would seem advisable to repeat the experiment.

Before an intelligent discussion of various alternative possible mechanisms can be made other quantitative experiments must be carried out. The present investigation does show, however, that under conditions such that the γ-bands are broadened, light of energy less than the higher value for the heat of dissociation photochemically decomposes NO, a fact that had been previously disputed.

APPENDICES

APPENDIX I. The servo slit-control mechanism on the Shell vacuum prism spectrometer.

In automatic recording spectrographs it is desirable to maintain a nearly constant background signal. This is most easily accomplished by having the slit width vary continuously as a function of wave length. This function is by no means simple since it depends upon such complicated factors as the dispersion of the prism and energy distribution in the light emitted by the source.

The vacuum prism spectrograph recently presented to us by the Shell Development Company arrived equipped with a slit drive mechanism controlled by a mechanical cam. The cam operated a set of breaker points which allowed a discontinuous current to flow to the slit drive motor. This arrangement was evidentally satisfactory when the spectrograph employed a direct current detector, but when an AC thermocouple was installed, the sudden making or breaking of contact at the breaker points set up interference which was picked up by the detecting system and appeared as relatively large random fluctuations on the recorded tracings. Although shielding the breaker points and motor with iron decreased this noise, it was still of roughly five times as large an amplitude as that inherent in the thermocouple. It soon became apparent that more effective shielding was not the best method of eliminating this noise, but instead a new mechanism void of sudden current surges should replace the old breaker points.

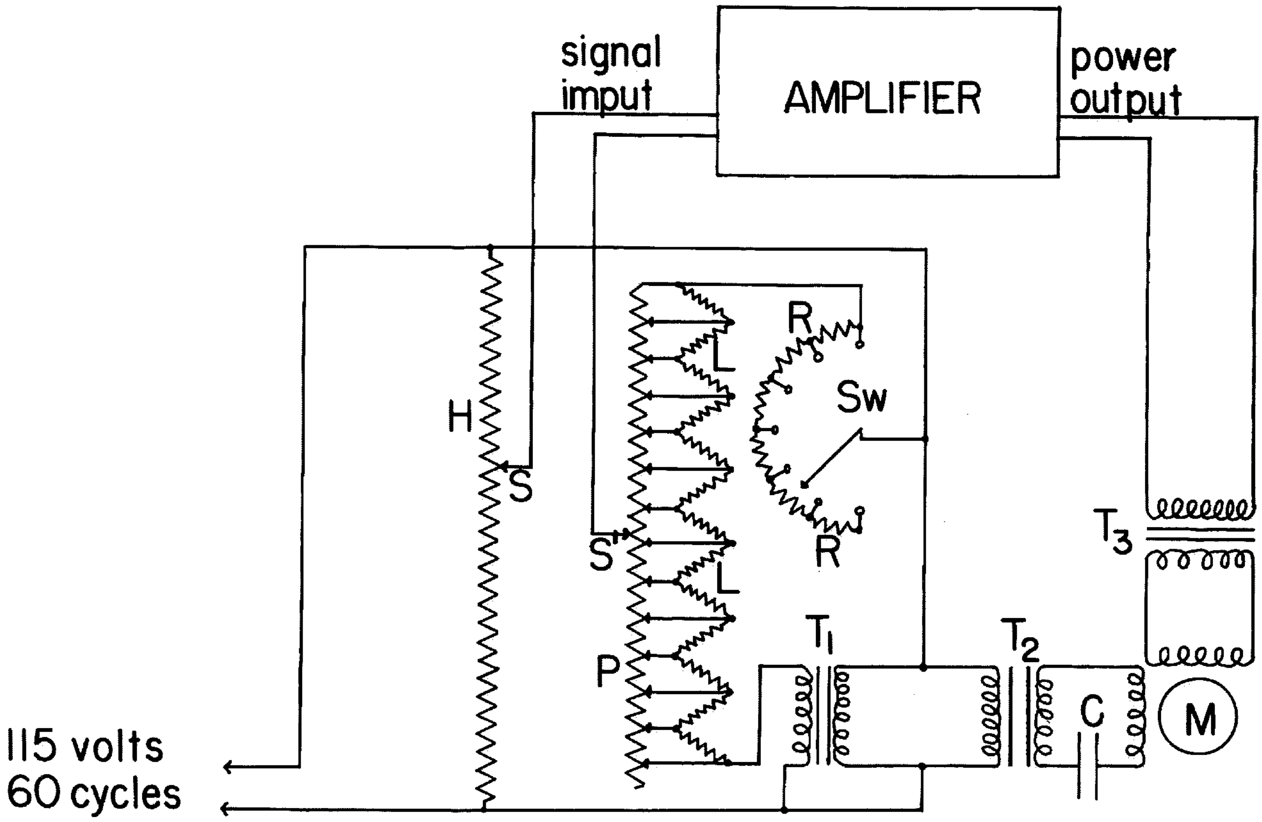
The mechanism chosen employs a servo motor and is found not to interfere with the detecting system. It has the added advantage of allowing a selection among several slit width schedules, adding to the versatility of the instrument.

Figure 11 shows a schematic diagram of the electrical system employed. The circular slide wire potentiometer P is geared directly to the prism table drive mechanism. Contact S is arranged to run linearly along Helipot H as the slit is opened or closed. By employing a proper phase angle between amplifier output and the line voltage, the servo motor will operate in such a sense as to reduce the potential difference between S and S'. In this manner definite points on potentiometer P can be made to correspond to particular slit openings.

In order to get the desired constant background intensity one must make potentiometer P non-linear. This was accomplished by connecting loading resistors L of appropriate values. For the different prisms one can interchange sets of loading resistors by means of a multiple-contact plug and socket arrangement.

The set of resistors R in series with slide wire potentiometer P allows one to select any of several slit width schedules all of which give the same shape background. One point on P must always have the potential corresponding to the slit exactly closed. Transformer T_1 serves to maintain one end of P at such a constant potential.

Originally we attempted to use an amplifier circuit like that employed by the Perkin-Elmer Corporation for a similar purpose. It was necessary, however, to modify their design extensively before our servo operated.



C	Phase shifter to give approximately 90° phase shift.
H	Ten turn Helipot (5kΩ) geared to slit drive motor.
L	Loading resistors to introduce desired degree of non-linearity to P.
M	Servo motor.
P	Circular potentiometer slide wire (5kΩ) geared to prism drive.
R	Resistors to increase or decrease slit widths by constant ratios throughout spectrum.
S,S'	Sliding contacts on P and H such that a signal is fed to the amplifier when S and S' are at different potentials.
Sw	Multiple position switch.
T_1	Transformer to maintain fixed potential to point on P corresponding to slit completely closed.
T_2	Transformer to reduce line voltage for 20 volt motor.
T_3	Load transformer to reduce amplifier output to 15-20 volts.

Figure 11. Schematic diagram of servo circuit.

APPENDIX II. Fitting a potential function to the hindered rotation about the N-O bond in nitrous acid.

Identifying the various parameters as in Figure 12, define θ_i

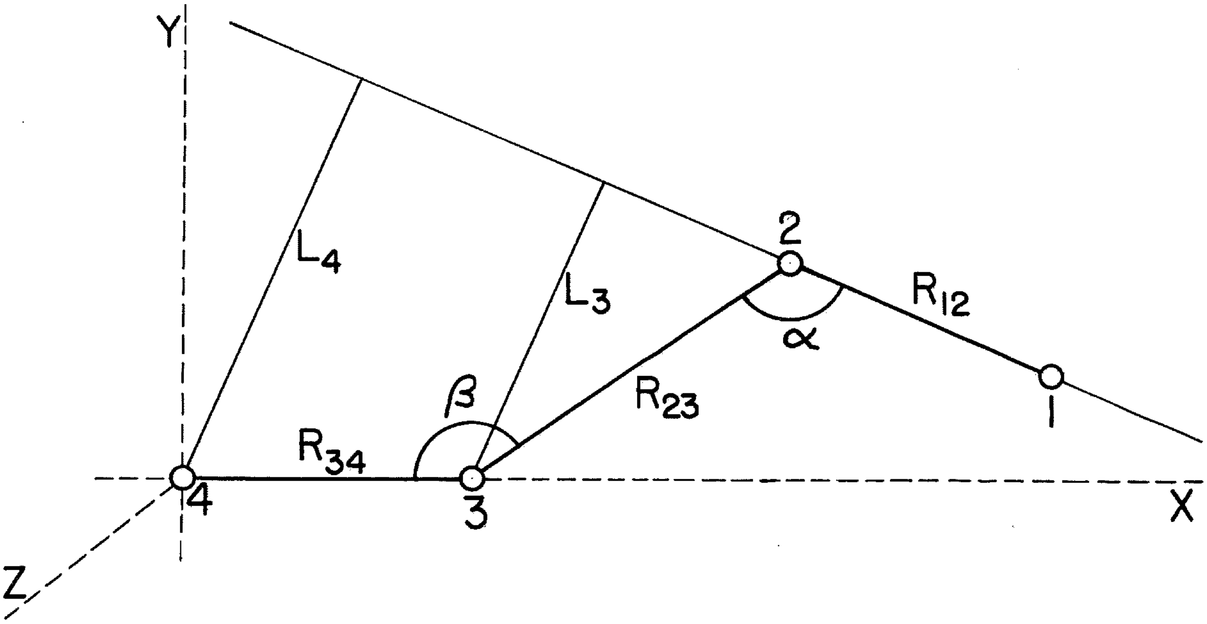


Figure 12

as the change in torsional angle when atom i is moved out of the xy plane a small distance z. Then

$$\theta_1 = Z_1/(R_{12}\ \sin\alpha),$$

$$\theta_2 = -Z_2\ (Y_1/Y_2)/(R_{12}\ \sin\alpha),$$

$$\theta_3 = -Z_3\ (L_4/L_3)/(R_{34}\ \sin\beta),$$

and $$\theta_4 = Z_4/(R_{34}\ \sin\beta).$$

Substituting for Y_1, Y_2, L_3 and L_4 in terms of R_{ij}, α and β, for an arbitrary small displacement from planarity the torsional angle changes by

$$\Delta\theta = (1/(R_{12}\ \sin\alpha))Z_1 - (1/(R_{12}\ \sin\alpha))(1+(R_{12}/R_{23})(\sin\ \alpha-\beta/\sin\beta))Z_2$$
$$- (1/R_{34}\ \sin\beta)(1+(R_{34}/R_{23})(\sin\beta-\alpha/\sin\alpha))Z_3 + (1/(R_{34}\ \sin\beta))Z_4.$$

Define $A_1 = 1$, $A_2 = Z_2/Z_1$, $A_3 = Z_3/Z_1$, and $A_4 = Z_4/Z_1$, then $dZ_2/dZ_1 = A_2$,

$dZ_3/dZ_1 = A_3$ and $dZ_4/dZ_1 = A_4$. Now

$$\Delta\theta = DZ_1$$

where

$$D = (1/R_{12} \sin\alpha)A_1 - (1/R_{12} \sin\alpha)(1 + (R_{12}/R_{23})(\sin\alpha-\beta / \sin\beta))A_2 - (1/R_{34} \sin\beta)(1 + (R_{34}/R_{23})(\sin\beta-\alpha/\sin\alpha))A_3 + (1/R_{34} \sin\beta)A_4$$

Now write down the Lagrangian for this out of plane oscillation:

Potential energy $\equiv V = \frac{1}{2}k_\tau \theta^2$, where k_τ is an effective force constant.

Kinetic energy $\equiv T = \frac{1}{2}\sum_{i=1}^{4} M_i \dot{Z}_i^2 = \frac{1}{2}\sum M_i(A_i\dot{Z}_i)^2 = \frac{1}{2}\sum M_i(A_i\dot{\theta}/D)^2$.

$L = T - V = \frac{1}{2}(\dot{\theta}/D)^2 \sum M_iA_i^2 - \frac{1}{2}k_\tau\theta^2$.

The equation of motion is

$$\ddot{\theta} + (k_\tau D^2/\sum M_iA_i^2)\theta = 0$$

The frequency of the vibration and the force constant are given by

$$\bar{\nu} = (D/2\pi)\ (k_\tau/\sum M_iA_i^2)^{\frac{1}{2}}$$

$$k_\tau = 4\pi^2\bar{\nu}^2 \sum M_iA_i/D^2.$$

Therefore

$$V = (2\pi^2\bar{\nu}^2 \sum M_iA_i^2/D^2)\theta^2$$

and $$d^2V/d\theta^2 = 4\pi^2\bar{\nu}^2 \sum M_iA_i^2/D^2$$

In order to evaluate the A_i's and hence D consider the conservation of momentum equations. From the condition that the vibration results in no net translational momentum along the Z axis one has

$$\sum_{i=1}^{4} M_i\dot{Z}_i = 0$$

From the conditions that no angular momenta about the Y and X axes shall result, one gets

$$\sum M_iX_i\dot{Z}_i = 0 \quad \text{and} \quad \sum M_iY_i\dot{Z}_i = 0,\ \text{respectively.}$$

Dividing through by $\dot{Z}_1$ these can be put in the form

$$M_2A_2 + M_3A_3 + M_4A_4 = - M_1$$

$$M_2X_2A_2 + M_3X_3A_3 + M_4X_4A_4 = - M_1X_1$$

$$M_2Y_2A_2 + M_3Y_3A_3 + M_4Y_4A_4 = - M_1Y_1$$

These simultaneous equations may be solved for A_2, A_3 and A_4 to yield

$$A_2 = - \frac{M_1}{M_2} \frac{(X_3 - X_1)(Y_4 - Y_1) - (X_4 - X_1)(Y_3 - Y_1)}{(X_2 - X_4)(Y_2 - Y_3) - (X_2 - X_3)(Y_2 - Y_4)}$$

$$A_3 = - \frac{M_1}{M_3} \frac{(X_2 - X_4)(Y_2 - Y_1) - (X_2 - X_1)(Y_2 - Y_4)}{(X_2 - X_4)(Y_2 - Y_3) - (X_2 - X_3)(Y_2 - Y_4)}$$

$$A_4 = - \frac{M_1}{M_4} \frac{(X_2 - X_1)(Y_2 - Y_3) - (X_2 - X_3)(Y_2 - Y_1)}{(X_2 - X_4)(Y_2 - Y_3) - (X_2 - X_3)(Y_2 - Y_4)} .$$

Inserting the values of the coordinates calculated from the parameters for cis and trans nitrous acids (Table VI), one obtains

$$\frac{d^2V}{d\theta^2} = 26.4 \text{ kcal mole}^{-1} \text{ radian}^{-2} \text{ for cis}$$

$$= 19.2 \text{ kcal mole}^{-1} \text{ radian}^{-2} \text{ for trans.}$$

Consider a potential function of the form

$$V = C_0 + C_1 \cos\theta + C_2 \cos 2\theta + C_3 \cos 3\theta.$$

Using the boundary conditions

at $\theta = 0$, $V = 0$, $dV/d\theta = 0$ and $d^2V/d\theta^2 = 19.20$ and

at $\theta = \pi$, $V = 0.5$, $dV/d\theta = 0$ and $d^2V/d\theta^2 = 26.4$,

one finds

$C_0 = 5.96$ kcal mole^{-1}

$C_1 = -0.745$ " "

$C_2 = -5.70$ " "

$C_3 = 0.483$ " " .

The potential function relative to the trans configuration is

$$V(\text{kcal mole}^{-1}) = 5.96 - 0.745 \cos\theta - 5.70 \cos 2\theta + 0.483 \cos 3\theta.$$

At $\theta = 95^{\circ}$ this function has a maximum of 11.76 kcal.

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PROPOSITIONS

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1. The photochemical decomposition of nitric oxide by absorption to the lower vibrational levels of the upper electronic state of the γ-system (1) should be investigated in detail.

    (1). G. E. Moore, this thesis, section II.

2. Organic isocyanides hydrolyze very rapidly in acid but are unaffected by alkali, in contrast to the thermodynamically more stable nitriles, which are hydrolysed by both acid and base. I propose a mechanism for the hydrolysis of the isocyanides that explains this inertness toward OH^-.

3. Observation under high dispersion of the N_2O_4 band near 4810 cm^{-1} is sufficient to distinguish between a planar configuration and a configuration with NO_2 groups in mutually perpendicular planes (Vd).

4. The bands in the visible region observed in a discharge in flowing nitric oxide (1) have not been definitely assigned. I propose that these bands are members of the previously unobserved quartet system of NO.

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5. The magnitude of the inconsistencies which arise when molecular parameters are calculated from the usual microwave data (1) can be significantly improved by employing heated wave guides.

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6. The kinetics of the gas-phase reaction of hydroiodic acid and dialkyl peroxides should be investigated.

7. The predissociation observed in NO (1) is inconsistent with the heat of formation of NO from N_2 and O_2.

   (1). L. Gero and R. Schmid, Proc. Phys. Soc. (London) 60, 533 (1948).

8. Contrary to the conclusions of Lord and Merrifield (1), the behavior of the N-H stretching frequencies in the tertiary amine salts can be shown to be consistent with a simple electrostatic picture of the interaction between the hydrogen and halide atoms.

   (1). R. C. Lord and R. E. Merrifield, J. Chem. Phys. 21, 166, (1953).

9. Rundle (1) suggests that the change in unit cell dimensions of ice and heavy ice with temperature offers a test of the theory advanced by Nordman and Lipscomb (2) to explain the lengthening of strong hydrogen bonds on deuterium substitution. I propose

   a) that this change does not test the theory

   b) that the theory does not explain the lengthening.

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   (2). C. E. Nordman and W. N. Lipscomb, J. Chem. Phys. 19, 1422 (1951).

10. To alleviate the shortage of chemists, especially physical chemists, a laboratory course in explosives and pyrotechnics should be included in the high school curriculum.