

The Vibrational Spectra and Structure of Inorganic Molecules. III. The InfraRed Spectra of Nitrosyl Chloride and Nitrosyl Bromide from 2.0 to 25 μ

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The Vibrational Spectra and Structure of Inorganic Molecules. III. The Infra-Red Spectra of Nitrosyl Chloride and Nitrosyl Bromide from 2.0 to 25 μ *

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(Received August 30, 1950)

The infra-red absorption spectra of nitrosyl chloride and nitrosyl bromide vapors have been examined from 400 to 5303 cm^{-1} , and the spectra explained on the basis of three fundamentals at 1799, 592, and 332 cm^{-1} for NOCl and 1801, 542, and 265 cm^{-1} for NOBr. The force constants and the amplitudes for the fundamental modes were calculated for a central force system. The $P-R$ separation of the predominantly parallel bands and the spacing of rotational bands in one partially resolved mainly perpendicular band in the NOCl spectrum were found to be in good accord with the electron diffraction data for the dimensions of the molecule. Thermodynamic functions for the gases were calculated from 298° to 1500°K. The calculated values of S_{298}^0 for both gases are in good agreement with the experimental values.

I. NITROSYL CHLORIDE

THE infra-red absorption spectrum of NOCl gas has been measured previously by Bailey and Cassie¹ who interpreted their spectrum on the basis of three fundamentals, viz., $\nu_1 = 1832 \text{ cm}^{-1}$,

$$\nu_2 = 633 \text{ cm}^{-1}, \text{ and } \nu_3 = 923 \text{ cm}^{-1}.$$

These fundamentals were shown to be unsatisfactory by Beeson and Yost² from comparison of the observed entropy change for the reaction $2\text{NOCl}(g) \rightleftharpoons 2\text{NO} + \text{Cl}_2(g)$ with that calculated from the methods of statistical thermodynamics.³ If the fundamentals suggested by Bailey and Cassie are used to calculate the entropy change for this reaction it is found that $\Delta S^\circ(\text{calc.}) - \Delta S^\circ(\text{obs.}) = 3.6 \text{ cal./deg./mole}$. Since this is well outside the range of the experimental error of $\pm 0.3 \text{ cal./deg./mole}$ Beeson and Yost concluded that the band at 923 cm^{-1} was a combination of the fundamental at 633 cm^{-1} with a low lying bending frequency at $\sim 290 \text{ cm}^{-1}$. Using this revised assignment to calculate the entropy change for the reaction, gives $\Delta S^\circ(\text{calc.}) - \Delta S^\circ(\text{obs.}) = 0.4 \text{ cal./deg./mole}$.

The principal moments of inertia used in the above calculation of the entropy, viz.,

$$I_A = 9.05 \times 10^{-40} \text{ g cm}^2, \quad I_B = 147.7 \times 10^{-40} \text{ g cm}^2, \\ I_C = 156.7 \times 10^{-40} \text{ g cm}^2$$

were calculated from Ketelaar and Palmer's⁴ electron diffraction data, namely $r_{\text{ON}} = 1.14 \pm 0.02 \text{ \AA}$, $r_{\text{NCl}} = 1.95 \pm 0.01 \text{ \AA}$, and $\angle \text{O-N-Cl} = 116 \pm 2^\circ$.†

* Presented at the Symposium on Molecular Structure held at Columbus Ohio (June, 1950).

† National Research Laboratories Postdoctorate Fellow 1949-50.

¹ C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. **145A**, 336 (1934).

² C. M. Beeson and D. M. Yost, J. Chem. Phys. **7**, 44 (1939).

³ See G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 501 ff.

⁴ J. A. A. Ketelaar and K. J. Palmer, J. Am. Chem. Soc. **59**, 2629 (1937).

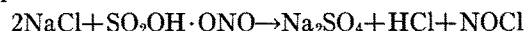
‡ The absorption of microwaves by NOCl³⁵ and NOCl³⁷ gives $I_B = 147.33$, $I_C = 152.59$, and $I_A = 5.27$ for NOCl³⁵ [Pietenpol, Rogers, and Williams, Phys. Rev. **77**, 741 (1950)]. These values for I_B and I_C and those obtained by electron diffraction are in

It is evident that the molecule is very nearly a symmetric top. However, since NOCl has a plane of symmetry, only all bands will be hybrid possessing perpendicular and parallel components. The fine structure spacing of the perpendicular component should be about 6 cm^{-1} which would be readily resolved under our experimental conditions.

This work was undertaken because of the tentative nature of the existing data with regard to choice of fundamentals, and also in the hope of resolving the perpendicular component of a band in order to find a spectroscopic value for the least moment of inertia.

Experimental

The nitrosyl chloride was prepared by the method of Tilden.⁵ Nitrosulfuric acid was dropped on dry sodium chloride and the gases evolved according to the equation



were collected in a trap immersed in molten chloroform (-63.5°C). The nitrosulfuric acid was prepared by absorbing the nitrosyl chloride obtained from heating aqua regia in concentrated sulfuric acid until the absorbing liquid was a golden brown color. The NOCl was purified in vacuum by keeping it immersed in a bath of solid CO_2 /acetone (-78°C) and pumping out the gases through a trap kept in a freezing mixture at -110°C . This caused an efficient separation from the more volatile impurities which did not condense and the less volatile, which remained in the vessel at -78°C . Five such distillations were carried out, rejecting the first and last fractions. Previous work⁶ has shown that this was sufficient to reduce the impurities to less than 0.26 percent.

The spectra were obtained with a Perkin-Elmer Model 12C infra-red spectrometer used in conjunction with a Brown recorder. The NOCl was introduced into

good agreement. The I_A obtained by these authors was calculated from $I_C = I_A + I_B$ which is only true for the instantaneous moments of inertia and not to be used here.

⁵ W. A. Tilden, J. Chem. Soc. **27**, 630 (1874).

⁶ F. S. Dainton and W. G. Burns (unpublished results).

TABLE I. The infra-red spectrum of NOCl gas.

Bailey and Cassie Obs.	Assignment	Obs.	This work PR separation	Assignment
		5303 ^a w		$3\nu_1=5397$
		4160 w	15	$2\nu_1+\nu_2=4160$
		3898 w	14	$2\nu_1+\nu_3=3900$
		3568 m	15	$2\nu_1=3598$
		2395 m PQR	18	$\nu_1+\nu_2=2391$
2155 m	$2\nu_2+\nu_3$	2131 m PQR	20	$\nu_1+\nu_3=2131$
1832 s	ν_1	1799 s PQR	19	ν_1
		1248 v.w.		$2\nu_3+\nu_2=1256$
1200 w	$2\nu_2$	1207 v.w.		$\nu_1-\nu_2=1207$
		1184 v.w.		$2\nu_2=1184$
923 s	ν_3	923 s PR	15	$\nu_2+\nu_3=924$
		664 v.w.		$2\nu_3=664$
633 s	ν_2	592 s PR	18	ν_2
		332 ^b		ν_3

^a The frequency of this band was calculated to be about 5303 cm⁻¹ from the observed bands for ν_1 and $2\nu_1$ and then used as a calibration point for this region. Its numerical value may be considerably in error.

^b Obtained from the combination tones $2\nu_3$, $\nu_2+\nu_3$, $\nu_1+\nu_3$, $2\nu_1+\nu_3$.

TABLE II. Fine structure of band at 664 cm⁻¹

Arbitrary numbering	cm ⁻¹
1	631.0
2	636.9
3	642.5
4	648.6
5	653.0
6	657(?)
7	666.5

the evacuated absorption cell (10 cm in length) from a side arm containing the solid or liquid in a small bulb. The different pressures required were obtained by immersing the bulb in baths of known temperatures and the pressure obtained from the vapor pressure data.⁶

Results and Discussion

Figure 1 shows the bands observed between 400 and 5300 cm⁻¹. Their frequencies are included in Table I (column 3) and the frequencies of the bands obtained by Bailey and Cassie are given in column 1 of Table I for comparison.

The very strong band at 1799 cm⁻¹ must be ascribed to a fundamental associated with the NO vibration since it is reasonably close to the fundamental observed in nitric oxide⁷ at 1875 cm⁻¹. By reason of its intensity, the band at 592 cm⁻¹ may be considered to be another fundamental. The next most intense bands are at 923 and 2131 cm⁻¹. If the band at 923 cm⁻¹ is assumed to be a fundamental, it is impossible to explain the relatively strong band at 2131 cm⁻¹ by a binary combination. The assignment $2\times 592+923=2107$ cm⁻¹ which corresponds to the assignment made by Bailey and Cassie, for the band at 2155 cm⁻¹ has a large negative anharmonicity and seems to be too intense for a ternary combination tone. The bands at 2131 and 923 cm⁻¹ are best explained as combination tones of the fundamentals at 1799 and

592 cm⁻¹ with an unobserved fundamental at 332 cm⁻¹. On this basis namely $\nu_1=1799$ cm⁻¹, $\nu_2=592$ cm⁻¹, and $\nu_3=332$ cm⁻¹ the assignment in Table I has been made.

From the values of the principal moments of inertia a pure parallel band would be expected to give the usual PQR contour with unresolvable fine structure and a PR separation⁸ of 18.5 cm⁻¹. On the other hand, a pure perpendicular band would have a rotational fine structure with a spacing of about 6 cm⁻¹. Since the molecule has a plane of symmetry only, the observed bands are hybrid with both parallel and perpendicular components. The fundamentals at 1799 and 592 cm⁻¹ and all the observed combination tones and overtones appear to have mainly parallel character with no fine structure. The observed separation of the PR maxima (19 ± 1 cm⁻¹) agrees quite well with the calculated separation⁸ of 18.5 cm⁻¹.

The force constants were calculated assuming a central force field using the equations of Radakovic⁹ and the molecular dimensions mentioned above. The values obtained are

$$f_{\text{NO}} = 13.97 \times 10^5 \text{ dynes per cm},$$

$$f_{\text{NCl}} = 1.92 \times 10^5 \text{ dynes per cm},$$

$$f_{\text{ClO}} = 1.30 \times 10^5 \text{ dynes per cm}.$$

The amplitudes of the motions of the atoms in the three fundamental modes of vibration were calculated from the same equation⁹ and are shown in Fig. 2. The amplitudes are drawn to a scale which is ten times as large as that for the molecular dimensions. Examination of Fig. 2 suggests that the only vibration in which the rate of change of dipole moment is predominantly perpendicular to the axis of least moment of inertia is the bending vibration $\nu_3=332$ cm⁻¹. The weak overtone at

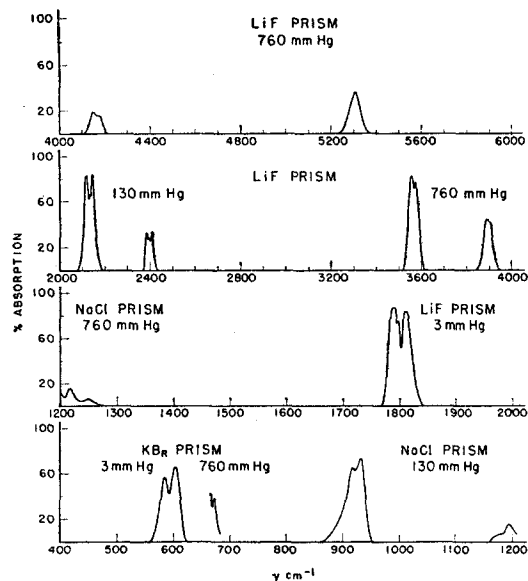


FIG. 1. Infra-red spectrum of gaseous NOCl.

⁸ S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).

⁹ M. Radakovic, Monats. f. Chem. **56**, 447 (1930).

⁷ R. H. Gillette and E. H. Eyster, Phys. Rev. **56**, 1113 (1939).

$\sim 664\text{ cm}^{-1}$ was examined at one atmosphere pressure for fine structure and the structure has been partially resolved (Fig. 3). The band is difficult to observe since it is overlapped on one side by the atmospheric CO_2 band at 667 cm^{-1} and on the other side by the tail of the very strong band at 592 cm^{-1} . Since the center of the band was not observed, the individual bands could not be numbered. Their frequencies are given in Table II. The spacing is about equal to the expected value of $\sim 6.0\text{ cm}^{-1}$. The fact that this overtone was observed and has the expected perpendicular character and the correct fine structure spacing is convincing confirmation of the assignment.

Thermodynamic Functions

Nitrosyl chloride gas is diamagnetic¹⁰ and the molecule appears to have a singlet ground state. On this basis and using the fundamentals given above and the electron diffraction values of the principal moments of inertia, the thermodynamic properties of the gas were calculated using the usual statistical-mechanical formulas. In Table III are listed the calculated values of C_p^0 , S^0 , and $-(F^0-H_0^0)/T$ for the gas from 300° to 1500°K . The calculated value of the entropy at 298°K , $S_{298}^0(\text{NOCl})_g = 62.4 \pm 0.1\text{ cal./deg./mole}$, agrees quite well with the observed value $S_{298}^0(\text{obs.}) = 63.0 \pm 0.3\text{ cal./deg./mole}$.

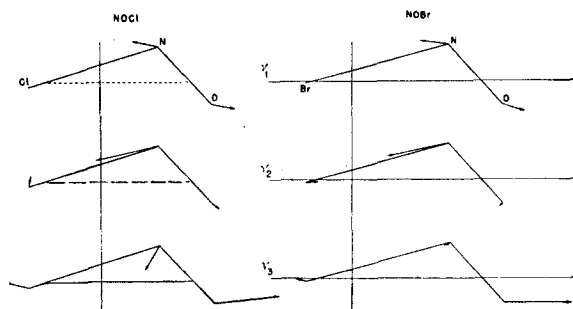
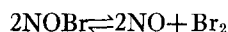


FIG. 2. The amplitudes during the modes of vibration of NOCl and NOBr.

II. NITROSYL BROMIDE

The electron diffraction experiments on nitrosyl bromide give the structure $\text{N}-\text{Br} = 2.14 \pm 0.02\text{ \AA}$, $\text{N}-\text{O} = 1.15 \pm 0.01\text{ \AA}$, $\angle \text{O}-\text{N}-\text{Br} = 117 \pm 3^\circ$. The infra-red spectrum has not been previously examined, but the entropy of the gas is available from measurements on the equilibrium¹¹



Experimental

Nitrosyl bromide was prepared by bubbling nitric oxide into bromine. The nitric oxide was prepared by

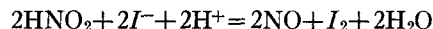
¹⁰ C. M. Beeson and C. D. Coryell, J. Chem. Phys. 6, 656 (1938).

¹¹ Blair, Brass, and Yost, J. Am. Chem. Soc. 56, 1916 (1934).

TABLE III. Thermodynamic functions of NOCl.

$T^\circ\text{K}$	$-(F^0-H_0^0)/T$ cal./deg./mole	S^0 cal./deg./mole	C_p^0 cal./deg./mole
298.2	53.291	62.386	10.628
300	53.345	62.450	10.640
350	54.837	64.184	10.954
400	56.031	65.496	11.218
450	57.169	66.931	11.449
500	58.208	68.149	11.658
600	60.048	70.306	12.019
700	61.652	72.183	12.320
800	63.074	73.845	12.566
900	64.355	75.338	12.768
1000	65.523	76.692	12.931
1100	66.595	77.930	13.065
1200	67.588	79.073	13.176
1300	68.513	80.131	13.267
1400	69.379	81.118	13.342
1500	70.192	82.040	13.405

the method given by Johnson and Giauque,¹² but without their stringent precautions for purity. The gases evolved in the reaction



were passed in turn through concentrated H_2SO_4 , 50 percent KOH, a trap at -78° , and P_2O_5 . The nitric oxide was passed next into a trap of bromine (reagent grade) and a mixing bulb, and the gases finally condensed in molten carbon tetrachloride at -23°C . This product was purified in the same manner as the nitrosyl chloride, the first trap being kept at -63.5°C in molten chloroform, and the second at -110°C . The nitrosyl bromide could not be freed from nitric oxide since the mixture of gases due to the above equilibrium contains about seven percent NO at one atmosphere pressure, and room temperature.¹¹ This was not serious since the spectrum of NO is well known⁷ and could be easily identified.

The same type of cell was used as for nitrosyl chloride. Only two pressures were used—a very low pres-

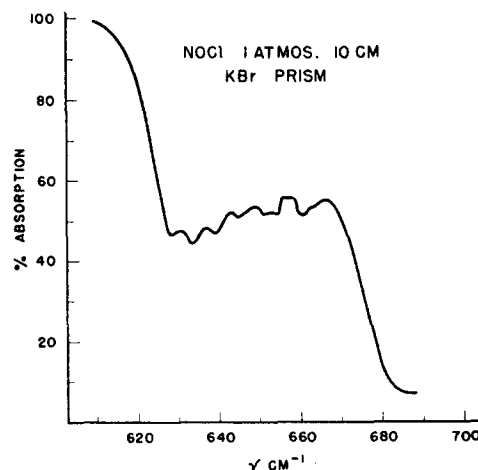


FIG. 3. Fine structure of $2v_3$ for NOCl.

¹² H. L. Johnson and W. F. Giauque, J. Am. Chem. Soc. 51, 3194 (1929).

TABLE IV. The infra-red spectrum of NOBr gas.

Obs. cm^{-1}	PR separation	Assignment
5303 ^a w		$3\nu_1 = 5403$
4103 w		$2\nu_1 + \nu_2 = 4109$
3831 w	14	$2\nu_1 + \nu_3 = 3832$
3567 w	15	$2\nu_1 = 3602$
2340 w	15	$\nu_1 + \nu_2 = 2343$
2066 w	15	$\nu_1 + \nu_3 = 2066$
1801 v.s.	15	ν_1
807 w	16	$\nu_2 + \nu_3 = 807$
542 v.s.	14	ν_2
265 ^b		ν_3

^a See footnote (a) to Table I.^b Obtained from the combination tones $\nu_2 + \nu_3$, $\nu_1 + \nu_3$, $2\nu_1 + \nu_2$.

TABLE V. Thermodynamic functions of NOBr.

$T^\circ\text{K}$	$-(F^\circ - H_0^\circ)/T$ cal./deg./mole	S° cal./deg./mole	C_p° cal./deg./mole
298.2	55.991	65.333	10.865
300	56.047	65.398	10.876
350	57.506	67.096	11.148
400	58.801	68.600	11.378
450	59.966	69.952	11.582
500	61.029	71.183	11.770
600	62.906	73.358	12.101
700	64.538	75.246	12.382
800	65.983	76.195	12.615
900	67.283	78.414	12.806
1000	68.465	79.771	12.963
1100	69.550	81.013	13.091
1200	70.553	82.157	13.198
1300	71.487	83.217	13.285
1400	72.362	84.205	13.359
1500	73.182	85.128	13.420

sure estimated at 5 mm for the fundamentals, and a pressure of one atmosphere which was required for the overtones and combinations, as the spectrum was much less intense than that of the nitrosyl chloride.

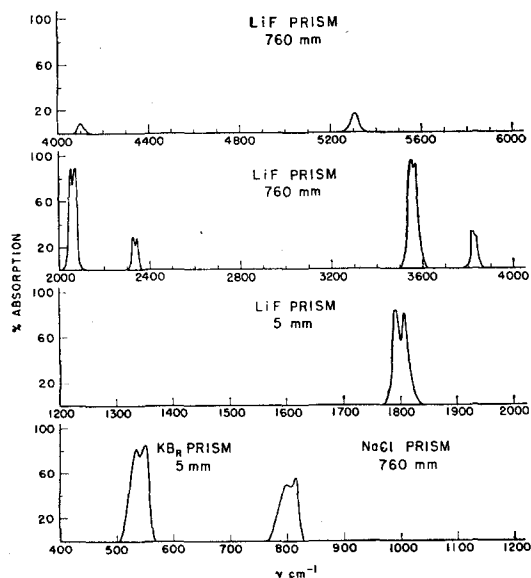


FIG. 4. Infra-red spectrum of gaseous NOBr.

TABLE VI. Comparison of the spectra of NOCl and NOBr.

NOCl cm^{-1}	Assignment	NOBr cm^{-1}
5303 w	$3\nu_1$	5303 w
4160 w	$2\nu_1 + \nu_2$	4103 w
3898 w	$2\nu_1 + \nu_3$	3831 w
3568 w	$2\nu_1$	3567 w
2395 m	$\nu_1 + \nu_2$	2340 w
2131 m	$\nu_1 + \nu_3$	2066 w
1799 v.s.	ν_1	1801 v.s.
1248 v.w.	$2\nu_2 + \nu_2$	
1207 v.w.	$\nu_1 - \nu_2$	
1184 v.w.	$2\nu_2$	
923 s	$\nu_2 + \nu_3$	807 w
~664 v.w.	$2\nu_3$	
592 v.s.	ν_2	542 v.s.
332	ν_3	265

TABLE VII. Comparison of some molecular properties of NOCl and NOBr.

Molecular property		NOCl	NOBr
Force constants in units of 10^6 dynes/cm	f_{N-O} f_{N-X} f_{O-X}	14.0 1.92 1.30	14.0 2.18 0.832
Bond distances in angstroms and angle in degrees	R_{NO} R_{N-X} $\angle ONX$	1.14 ± 0.02 1.95 ± 0.01 $116 \pm 2^\circ$	1.15 ± 0.04 2.14 ± 0.02 $117 \pm 3^\circ$
Moments of inertia in 10^{-40} c.g.s. units	I_A I_B I_C	9.05 147.7 156.7	9.40 229.7 239.1
Frequencies of fundamentals in cm^{-1}	ν_1 ν_2 ν_3	1799 592 332	1801 542 265
Entropy in cal./deg./mole	$S^\circ_{298}(\text{calc.})$ $S^\circ_{298}(\text{obs.})$	62.4 ± 0.1 63.0 ± 0.3	65.3 ± 0.1 65.2 ± 0.3

Results and Discussion

Figure 4 shows the bands observed between 400 and 5300 cm^{-1} and Table IV gives the frequencies and the assignment.

Assignment

The assignment follows the same argument as for nitrosyl chloride, since the spectra are very similar. It is even more unlikely with nitrosyl bromide that the band at 807 cm^{-1} is a fundamental since its intensity is so much less than that of the bands at 542 and 1801 cm^{-1} .

Discussion

The principal moments of inertia, calculated from the electron diffraction measurements are

$$I_A = 9.40 \times 10^{-40} \text{ g cm}^2, \quad I_B = 229.6 \times 10^{-40} \text{ g cm}^2, \\ I_C = 239.0 \times 10^{-40} \text{ g cm}^2$$

so that a parallel band should have a PR separation⁸ of

14.6 cm^{-1} , and a perpendicular band should have resolvable fine structure with a separation of $\sim 6 \text{ cm}^{-1}$. The force constants were calculated for a central force field⁹ as for nitrosyl chloride, and the values obtained were

$$\begin{aligned}f_{\text{NO}} &= 14.00 \times 10^5 \text{ dynes per cm,} \\f_{\text{NBr}} &= 2.18 \times 10^5 \text{ dynes per cm,} \\f_{\text{BrO}} &= 0.832 \times 10^5 \text{ dynes per cm.}\end{aligned}$$

The amplitudes of the vibrations of the atoms were calculated as for the nitrosyl chloride, and are shown in Fig. 2. No band appears to be predominantly perpendicular. The overtone of 265 cm^{-1} is masked by the strong fundamental at 542 cm^{-1} . All the combination tones were found to be parallel in character, as were the other two fundamentals, and no fine structure was resolved. The observed separation of the *PR* maxima of $15 \pm 1 \text{ cm}^{-1}$ agrees quite well with the value 14.6 cm^{-1} calculated by the method of Gerhard and Dennison.⁸

Thermodynamic Functions

Using the usual statistical equations, and assuming the usual harmonic oscillator rigid rotator approximation, the values of S^0 , C_p^0 , and $-(F^0 - H_0^0)/T$ were calculated for the gas and are given in Table V. The calculated value of the entropy at room temperature, 65.3 cal./deg./mole, agrees well with the value (65.2 ± 0.3 cal./deg./mole) obtained by Blair, Brass, and Yost¹¹ from measurements of the equilibrium with nitric oxide and bromine.

A comparison of the spectra of NOCl and NOBr is given in Table VI.

Some of the molecular constants and properties of NOCl and NOBr are compared in Table VII.

The authors are indebted to Miss E. Miller for reduction of the spectra and computational assistance.

Note added in proof: A note on the infra-red spectrum of NOCl has appeared [J. H. Wise and J. T. Elmer, *J. Chem. Phys.* **18**, 1411, 1950] while our manuscript was in press. The results are in agreement with our conclusions for this molecule.

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The Multiplicity Forbidden Absorption Bands in the Spectrum of Pyridine

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(Received August 11, 1950)

The two singlet-triplet transitions of pyridine have been studied using very long optical paths. The first of these, a π -electron transition, which was previously observed in the liquid phase only as a region of continuous weak absorption at the long wave end of the main absorption system, has been observed in the gas phase as a well-defined band system between 3000 and 3300 Å with a maximum molar absorption coefficient, $\epsilon = 0.10$.

The sixty observed bands have been fitted into a vibrational scheme which suggests that the transition responsible for them is allowed by symmetry.

The second transition which involves the non-bonding pair of electrons on the nitrogen atom was observed previously as a low temperature phosphorescence emission. Attempts to observe this transition in absorption using very long paths in the gas phase were unsuccessful, but it has been observed weakly using an optical path of 45 cm of liquid pyridine.

INTRODUCTION

THE ultraviolet absorption spectrum of gaseous pyridine has been investigated by Henri and Angenot,¹ by Sponer and Stucklen,² and by Lord.³ The band of lowest wave number observed by any of these investigators was that at 32488 cm^{-1} , denoted by Henri and Angenot as "extremely weak" when observed with a path length of 53 cm and a pressure of 900 mm of pyridine vapor. The system of bands between 32500 and 38500 cm^{-1} will be henceforth referred to as the Henri-Angenot bands.

Two observations have been made at lower fre-

quencies.⁴ Low temperature phosphorescence emission was observed with a high frequency limit at about 25000 cm^{-1} and was identified as due to the lowest triplet \rightarrow singlet transition involving the non-bonding electron pair on the N atom. In the region 29000 to 33000 cm^{-1} a very weak continuous absorption was observed in 5 cm of liquid pyridine. This was identified as due to a transition from the ground (singlet) state to a second triplet state involving π -electron excitation analogous to the well-known singlet-triplet absorption of benzene.

It appeared of interest to see whether, by using the very long absorption paths now available, these transi-

¹ V. Henri and P. Angenot, *J. de Chem. Phys.* **33**, 641 (1936).

² H. Sponer and H. Stucklen, *J. Chem. Phys.* **14**, 101 (1946).

³ R. C. Lord (private communication).

⁴ M. Kasha and C. Reid, " π - and n -electron transitions in N heterocyclics" (in preparation).