

Coulson,<sup>12</sup> on the basis of theoretical studies, has shown that the carbon atom is the positive end of the dipole. On the other hand, Cole and Thompson<sup>13</sup> have used measurements on the extinction coefficients of benzene derivatives in solution to prove that the hydrogen is the positive atom. Gent,<sup>14</sup> in a survey on the polarity of the C—H bond, points out that there is very possibly a reversal of polarity from methane to acetylene, and that the carbon end of the bond is likely to be negative in acetylene but positive in methane.

From dispersion measurements on methane, Rollefson and Havens<sup>3</sup> found the C—H bond moment to be  $0.307D$ . For the out-of-plane bending in ethylene, Hammer<sup>4</sup> calculated a moment of  $0.629D$ . (For other vibrations, values of 0.72 and  $0.315D$  were obtained.) The effective charge for the stretching vibrations was approximately  $0.5 \times 10^{-10}$  esu for each of the three

<sup>12</sup> C. A. Coulson, *Trans. Faraday Soc.* **38**, 433 (1942).

<sup>13</sup> A. R. H. Cole and H. W. Thompson, *Trans. Faraday Soc.* **46**, 103 (1950).

<sup>14</sup> W. L. G. Gent, *Quart. Rev.* **2**, 383 (1948).

hydrocarbons. It appears from this research that the magnitude of the C—H bond shows some regularity, being almost in the ratio 1:2:3 as the carbon-carbon link goes from zero to double to triple bonding, although this regularity may be entirely accidental, since the signs may not be the same.

An additional item of interest is the extrapolation of the refractive index to infinite wavelength, where  $\epsilon = n^2$ . Watson, Rao, and Ramaswamy<sup>15</sup> have measured essentially the static dielectric constant, obtaining the value  $\epsilon - 1 = 1330 \times 10^{-6}$  after reduction to 0°C. From Eq. (3),  $(n_0 - 1)_\infty = 661.71 \times 10^{-6}$  or  $(n_0^2 - 1)_\infty = 1323.9 \times 10^{-6}$ . The difference between  $n^2$  and  $\epsilon$  is only  $6 \times 10^{-6}$ , which is within the limits of experimental error. The contributions of the infrared bands thus completely account for the difference between the dielectric constant and the square of the refractive index extrapolated to zero frequency from the visible.

<sup>15</sup> Watson, Rao, and Ramaswamy, *Proc. Roy. Soc. (London)* **143A**, 558 (1934).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 19, NUMBER 12 DECEMBER, 1951

## The Infrared Spectrum and the Structure of Gaseous Nitrous Acid\*

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(Received September 5, 1951)

An investigation of the infrared spectrum of nitrous acid has shown that in the gaseous state this substance exists in two tautomeric species which are believed to be *trans*- and *cis*-forms. The *cis*-form is of higher energy by about 506 calories mole<sup>-1</sup>. A complete vibrational analysis is given and the OH in plane bending frequencies are found to be 1260 cm<sup>-1</sup> and ~1292 cm<sup>-1</sup>, and the out of plane frequencies 543 cm<sup>-1</sup> and 637 cm<sup>-1</sup> for the *trans*- and *cis*-molecules, respectively. From the rotational constants the O—N—O angle is estimated to be 118° for the *trans*-form and 114° for the *cis*-form, from which conclusions are drawn regarding the electronic structure of the molecule. The standard entropy of nitrous acid at 25° is calculated.

### INTRODUCTION

TO the best of our knowledge the only previous observation on the infrared spectrum of nitrous acid was made by E. J. Jones<sup>1</sup> who observed what appeared to be a double band in the  $1.4\mu$  region. This he explained as due to the presence of two isomeric forms of the acid. Strangely enough an investigation recently completed in this laboratory has shown that this belief of Jones is indeed correct though it was not at all justified by his observations. He had observed merely the *P* and *R* branches of a single *A* type band, of which the central *Q* branch was not evident, probably because of the lack of resolving power of his spectrometer. Our investigation has encountered some unusual problems, but has been very rewarding as the experimental results finally all appear to fit into a very plausible pattern.

### EXPERIMENTAL PROCEDURES

Since the equilibrium between nitrous acid, NO, NO<sub>2</sub>, and water vapor is very rapidly established it was not possible to study the first substance in the pure state and it was necessary to investigate an equilibrium mixture. Such a mixture may contain a considerable number of species which have strong absorption bands and may produce considerable interference. It was consequently necessary to identify all bands due to contaminants and to choose conditions such that interference from this source was at a minimum. A typical mixture employed contained NO and NO<sub>2</sub> at partial pressures of 570 mm and 15 mm, respectively, and the vapor of water, or of heavy water, at the saturation pressure at 25°C. With the use of existing thermodynamic data<sup>2</sup> this mixture was estimated to contain

\* Contribution No. 1630.

<sup>1</sup> E. J. Jones, *J. Am. Chem. Soc.* **65**, 2274 (1943).

<sup>2</sup> For references see L. G. Wayne and D. M. Yost, *J. Chem. Phys.* **19**, 41 (1951).

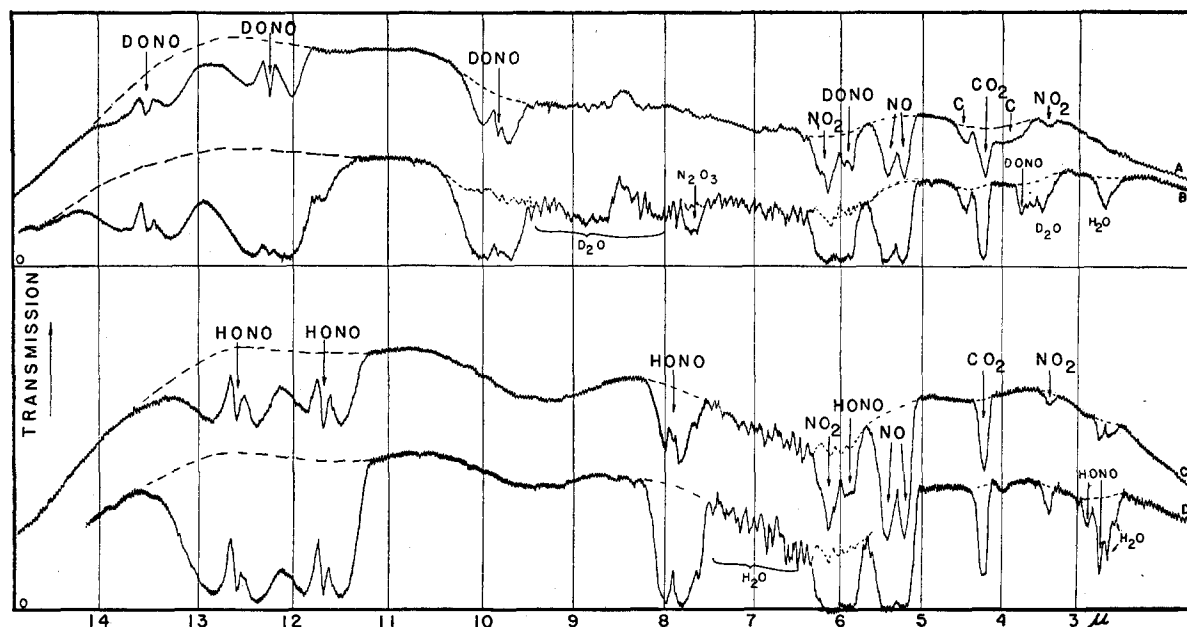


FIG. 1. Prismatic spectrum of heavy and light nitrous acid in the NaCl region. The absorptions indicated by C are definitely due to contaminants. Nitrous acid pressure was 2-3 mm throughout, path length was 5 cm in curves A and C and 50 cm in curves B and D.

nitrous acid at a pressure of about 18 mm, together with traces of  $N_2O_3$  and nitric acid.

The spectra were mapped under low dispersion from 2-15 $\mu$  with a Beckmann IR-2 spectrometer equipped for recording, and provided with a simple automatic slit control which keeps the background intensity reasonably constant through this region. In the region 14-25 $\mu$  a vacuum spectrometer<sup>3</sup> with potassium bromide optics was employed. The fine structure investigation of the O-H fundamentals, overtones and combination bands out to 3.2 $\mu$  was made with a vacuum grating spectrometer previously described.<sup>4</sup> A selected lead sulfide photoconductive cell cooled with solid  $CO_2$  was employed as detector. The water vapor lines, recently measured with high accuracy by R. C. Nelson<sup>5</sup> were used for wavelength calibration.

#### EXPERIMENTAL RESULTS

The prismatic spectra of nitrous acid and of deuterio nitrous acid are shown in Figs. 1 and 2. Portions of the region investigated with high dispersion are represented in Figs. 3-5. In Table I are given the frequencies of band origins, together with a description of the bands and assignments.

#### INTERPRETATION

The spectrum of nitrous acid exhibits several unusual features of which the most striking is the duplication of many of the more intense bands which one appears

obliged to attribute to the presence of two tautomeric forms. This is most immediately evident in the region of the O-H stretching frequencies and their overtones.

In both fundamental and overtone regions two rather intense bands appear in the spectra of both light and heavy nitrous acid. The more intense of these is in each case an A type band, while the other has hybrid structure but is predominately of B type. The frequency difference between the two bands in the overtone region is approximately twice that in the fundamental region, and the isotope shift of all four bands is well within the range to be expected for hydrogen valence frequencies. These facts appear to exclude the possibility that any of the bands could be assigned to a combination tone, and indicate that there are indeed two O-H stretching fundamentals.

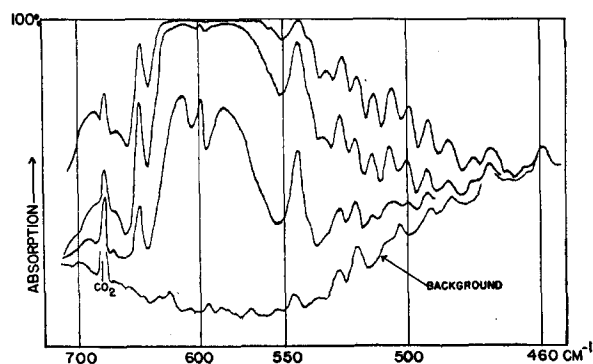


FIG. 2. Prismatic spectrum of nitrous acid in the KBr region: The weak lines in the background spectrum, except for the  $CO_2$  maximum, are due to water which was present to the same amount in all spectra.

<sup>3</sup> A recent gift from the Shell Development Company. For description see R. R. Brattain, *Phys. Rev.* **60**, 164 (1941).

<sup>4</sup> Badger, Zumwalt, and Giguère, *Rev. Sci. Instr.* **19**, 861 (1948).

<sup>5</sup> R. C. Nelson, Summary Report No. IV, Contract NObs 28373, Dept. Physics, Northwestern University.

We attribute the fundamental of lower frequency to a *cis*-form of nitrous acid and that of higher frequency to a *trans*-form (see Figs. 6(a) and (b)). This assignment was first suggested by the band types and is strongly supported by the rotational constants. The possibility that a nitro form (Fig. 6(c)) may occur has been considered, but for several reasons it seems evident that such a form does not contribute to the spectrum. A nitro form would almost certainly be planar and its N—H fundamental band would consequently be of pure *B* type. Although one of the observed fundamental bands is predominantly of *B* type it is actually a hybrid as it quite definitely has a weak central *Q* branch. Furthermore, the change of rotational constant with deuterium substitution seems quite impossible to account for with a nitro model although it is perfectly compatible with the *cis*-structure.

#### TEMPERATURE EFFECT

It is immediately evident that the spectrum of nitrous acid in the region 5–25 $\mu$  contains too many bands to

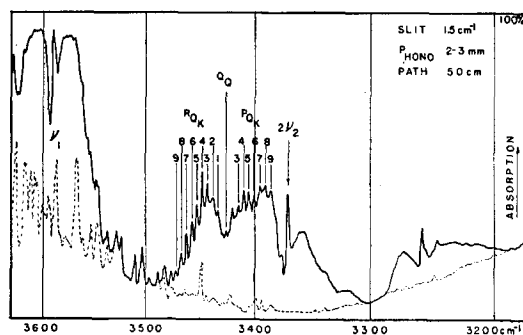


FIG. 3. Bands of *cis*- and *trans*-nitrous acid in the 3 $\mu$  region.

be ascribed to one molecule but in the beginning it was by no means obvious how they were to be apportioned to two molecular species. It is now clear that this can be done for the most part on the basis of intensity. As will be shown later, the *trans*-tautomer is about three times as prevalent as the *cis*-form and its bands are correspondingly more intense and more numerous. There is, however, one important exception to this generalization, namely the pair of similar bands near 12 $\mu$ , which led us into great difficulty. This was not resolved until an investigation was made of the effect of temperature on the relative intensities of certain bands.

The temperature range in which it is practical to investigate nitrous acid is unfortunately not very great and in most cases the situation is rather unfavorable for observing small changes in the relative intensities of analogous bands. In the O—H overtones no effect could be detected with certainty in the range 10–65°C. Since the band envelopes are quite different and the rather high intensity ratio of corresponding bands is unfavorable, we could only conclude that the difference

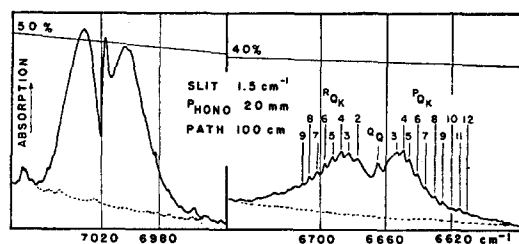


FIG. 4. First overtone of the O—H stretching vibration in *trans*- and *cis*-HONO.

in energy of the *trans*- and *cis*-tautomers is not large, probably not much greater than 350 cal mole<sup>-1</sup>.

Fortunately the pair of bands at 12 $\mu$  present a very favorable case owing to their practically identical envelopes and intensities. As shown in Fig. 7 a definite although small temperature effect was observed. The integrated intensity of 856 cm<sup>-1</sup> was found to increase relative to that of 794 cm<sup>-1</sup> by about 19 percent when the temperature was raised from 0° to 70°C. A similar effect was noticed with respect to the bands at 637 cm<sup>-1</sup> and 543 cm<sup>-1</sup>, whose intensity ratio was estimated to increase about 22 percent in the same temperature interval.

These estimates, although in reasonable agreement, may be considerably in error since there is considerable overlapping of bands, the band envelopes change somewhat with temperature, and the presence of overlapping contaminant bands could lead to error. We believe the last effect is absent and are convinced that the temperature effect is definitely real. The bands at 794 cm<sup>-1</sup> and 543 cm<sup>-1</sup> are consequently attributed to the *trans*-tautomer of lower energy which will later be identified as the *trans*-form. From the temperature effect the difference in energy of *cis*- and *trans*-forms is estimated to be 506 $\pm$ 250 cal mole<sup>-1</sup>.

#### ASSIGNMENT OF BANDS IN THE REGION 5–25 $\mu$

The assignment of 1696 cm<sup>-1</sup> and 1690 cm<sup>-1</sup> in light and heavy nitrous acid, respectively, to a double bond N=O valence vibration,  $\nu_2$ , seems straightforward. We believe that this is a *trans*-band and that the *cis*-fundamental of lower frequency and intensity is obscured by NO<sub>2</sub>, although its first overtone does appear. Because of the isotope shift we assign 1260 cm<sup>-1</sup> and 1018 cm<sup>-1</sup> to the hydrogen and deuterium bending vibrations in the plane of the molecule,  $\nu_3$ . The former

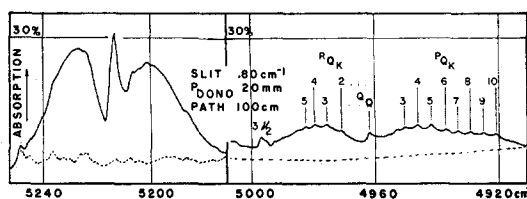


FIG. 5. First overtone of the O—D stretching vibration in *trans*- and *cis*-DONO.

band exhibits an extra maximum on the high frequency shoulder of its *R* branch which we believe represents the *R* branch of a weaker, partially overlapping band with center at about  $1292\text{ cm}^{-1}$ . Since the out of the plane hydrogen torsional frequency is found to be higher for the *cis*-tautomer it is plausible to attribute the (weaker) higher frequency in plane bending also to the *cis*-form. The corresponding band is not resolved in the DONO spectrum.

The bands at  $794\text{ cm}^{-1}$  and  $856\text{ cm}^{-1}$  are believed to represent the N—O single bond valence vibrations,  $\nu_4$ , of *trans*- and *cis*-tautomers, respectively, which are shifted to  $739\text{ cm}^{-1}$  and  $816\text{ cm}^{-1}$  in heavy nitrous acid. The above assignment to *cis*- and *trans*-forms is required by the temperature effect which shows that  $794\text{ cm}^{-1}$  originates in the same molecular species as  $543\text{ cm}^{-1}$ , which is definitely a *trans*-band. It is furthermore supported by the Teller-Redlich rule of isotope

TABLE I. Band centers and assignments in the spectrum of nitrous acid.

HONO		DONO		Band type	Assignment		Description
$\nu$ ( $\text{cm}^{-1}$ )	I	$\nu$ ( $\text{cm}^{-1}$ )	I		<i>cis</i>	<i>trans</i>	
543	80	416	60	C		$\nu_6$	H out of plane
598	120	591	120	A	( $\nu_5$ )?	$\nu_5$	O—N—O bend
637	50	508	40	C		$\nu_6$	H out of plane
794	100	739	40	A		$\nu_4$	O—N stretch
856	100	816	100	A		$\nu_4$	O—N stretch
1260	50	1018	60	A		$\nu_3$	O—H bend
~1292	~10?			A		$\nu_3$	O—H bend
1696	20	1690	20	?		$\nu_2$	O=N stretch
2505	2	...		?		$2\nu_3$	
3257	1	3196	0.5	A	$2\nu_2^a$		
3372	1.5	3361	1.5	A		$2\nu_2$	
3426	1.5	2530	1	$B(A)^b$	$\nu_1$		O—H stretch
3590	5	2650	3	A		$\nu_1$	
4124	0.0005			A		$\nu_2+2\nu_3$	
4378	0.001			A		$\nu_1+\nu_4$	
4830	0.02			A		$\nu_1+\nu_3$	
5038	0.002	4999		$B(A)^c$		$3\nu_2$	
6050	0.001			A		$\nu_1+2\nu_3$	
6664.8	0.03	4963		$B(A)^b$	$2\nu_1$		
7015	0.10	5212		A		$2\nu_1$	

<sup>a</sup> Assigned on the basis of intensity, frequency, and isotope shift. Fundamental estimated to be around  $1640$  in HONO and  $1610$  in DONO, obscured by  $\text{NO}_2$ .

<sup>b</sup> Hybrid, predominantly *B* type.

<sup>c</sup> DONO band is hybrid.

shift, which is poorly satisfied by an alternative assignment.

The band at  $543\text{ cm}^{-1}$  clearly has *C* type structure though one branch of the band is obscured. The structure and large isotope shift identify it as the OH torsional or out of the plane vibration. It is attributed to the *trans*-tautomer since the rotational spacing is much greater than that of the OH valence fundamental of the *cis*-species. The rotational structure of the companion band of the *cis*-species at  $637\text{ cm}^{-1}$  could not be resolved but the breadth of the band and its isotope shift identify it.

The remaining vibration is the O—N—O bending to which the most intense band in the spectrum is assigned. On deuteration the shift is from  $598\text{ cm}^{-1}$  to  $591\text{ cm}^{-1}$ . In this case again, only one band is observed for the two species.

The assignments of a number of combination bands are given in Table I.

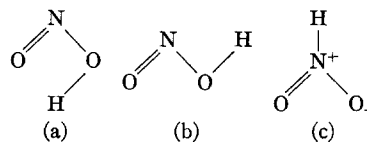


FIG. 6.

If the band origins are represented by the usual expression  $\nu = \sum v_i \omega_i + \sum \sum v_i v_j \chi_{ij}$  the following approximate values of convergence and interaction constants are found for the *trans*-tautomer of nitrous acid:

$$\chi_{11} = -83, \quad \chi_{11}(\text{DONO}) = -45, \quad \chi_{22} = -9, \quad \chi_{33} = -8, \\ \chi_{13} = -21, \quad \chi_{14} = -6, \quad \chi_{23} = -38.$$

Unless otherwise indicated these values refer to HONO.

### ROTATIONAL STRUCTURE

Details of the bands showing a resolvable rotational structure are given in Tables II and III. Unfortunately only the low frequency branch of the band at  $543\text{ cm}^{-1}$  was observable, which furthermore was contaminated with water lines, some of which practically coincide with HONO lines. The interference was not serious at high nitrous acid pressures and allowance was made for it in measuring the maxima. Because of the limits of KBr optics only the high frequency branch of the corresponding band for DONO was observed. In the latter case the central *Q* branch was observed but for some unexplained reason no rotational structure could be resolved, though strong continuous absorption was found from  $460\text{ cm}^{-1}$  to the limit of the KBr optics. Consequently the rotational constant for the *trans*-molecule is known only roughly, and only for HONO.

For the ground state of the *trans*-molecule we take the most probable value of the rotational constant  $A - (1/2)(B+C)$  to be  $2.40\text{ cm}^{-1}$  for *cis*-HONO,  $1.94\text{ cm}^{-1}$  for *cis*-DONO, and  $3.2\text{ cm}^{-1}$  for *trans*-HONO. Probable values for the moments of inertia of the various molecular species have been calculated from these constants and from estimated parameters and are given in a subsequent table.

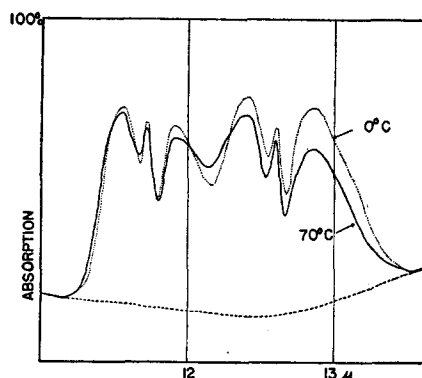


FIG. 7. The change of relative intensity with temperature of the  $856\text{ cm}^{-1}$  and  $794\text{ cm}^{-1}$  bands of *cis*- and *trans*-HONO.

TABLE II. Frequencies of the  $Q$  branches and combinations in the OH perpendicular bands of the *cis*-form of nitrous acid.

$K$	$PQ$	HONO $\nu_1 = 3426.1 \text{ cm}^{-1}$			$PQ$	HONO $2\nu_1 = 6664.8 \text{ cm}^{-1}$			$PQ$	DONO $2\nu_1 = 4962.8 \text{ cm}^{-1}$		
		$RQ$	$(A_0 - B_0)^a$	$(A_1 - B_1)$		$RQ$	$(A_0 - B_0)$	$(A_2 - B_2)$		$RQ$	$(A_0 - B_0)$	$(A_2 - B_2)$
0	...	...	...	...	...	...	...	...	...	...	...	...
1	...	3432.04	...	...	...	...	...	...	...	...	...	...
2	...	37.11	1.99	...	6658.19	6675.46	...	...	...	4972.11	...	...
3	3414.09	42.71	2.30	2.39	...	80.84	2.28	...	4953.65	76.23	1.87	1.88
4	09.52	47.24	2.35	2.36	48.06	85.90	2.30	2.37	49.68	79.88	1.92	1.89
5	05.17	52.29	2.35	2.36	44.08	91.18	2.35	2.36	45.43	83.44	1.94	1.90
6	00.19	56.86	2.38	2.36	38.98	95.63	2.40	2.36	50.99	...	1.95	...
7	3395.17	61.69	2.37	2.38	33.59	6700.51	2.40	2.39	36.65	...	...	...
8	90.53	66.54	2.38	2.38	28.50	05.19	2.40	2.40	37.52	...	...	...
9	85.56	70.86	2.38	2.37	23.64	09.98	2.40	...	...	...	...	...
10	80.97	...	2.38	...	18.67	...	...	...	...	...	...	...
11	75.70	...	...	...	13.70	...	2.41	...	...	...	...	...

<sup>a</sup>  $A_i - B_i$  is the rotational constant of the  $i$ th vibrational level when  $B_i = (1/2)(B_i + C_i)$ .

A comparison of the separation of the  $P$  and  $R$  maxima of the  $A$  type bands of the spectrum with that predicted from the moments of inertia above has shown that these bands have in reality considerable hybrid character. The presence of weak central branches in the *cis*-O-H bands has likewise shown this to be true of these apparently  $B$  type bands. Nevertheless it is remarkable, considering the lack of molecular symmetry, that bands of as nearly pure type are observed. This is particularly true of the bending fundamental at  $598 \text{ cm}^{-1}$  which is unexpectedly of  $A$  type. An explanation of this fact may be found in the electronic structure of the molecule discussed below.

#### THE STRUCTURE OF NITROUS ACID

The two parameters of the nitrous acid molecule which it would be most difficult to predict from previous experience are the O-N-O angle and the long O-N distance. Fortunately the choice of these quantities is very much restricted by the known rotational constants, which are relatively insensitive to the remaining parameters. We have consequently chosen to estimate the latter parameters by the comparison of force constants and frequencies with those of other molecules of known structure and to use the rotational constants to solve for the angle and distance mentioned above. The rotational constants are accounted for by the parameters given in Table IV.

The following arguments support the foregoing choice. The O-H distance was estimated from the O-H frequencies with the assistance of Badger's rule.<sup>6</sup> It can scarcely be in error by 0.01A. The choice of the HON angle is rather arbitrary and could be in considerable

TABLE III. Frequencies of maxima in the HONO band at  $543.2 \text{ cm}^{-1}$ .

$K$	$PQ$	$K$	$PQ$
1	(536.4)	6	505.4
2	530.8	7	498.9
3	523.5	8	492.4
4	517.7	9	486.0
5	(511.5)		

<sup>6</sup> R. M. Badger, J. Chem. Phys. 2, 128 (1934).

error since it has little effect on the rotational constants. However the change of rotational constant with deuterium substitution seems to exclude the possibility that it is as small as  $90^\circ$ . The angle has been taken somewhat smaller in the *cis*-modification in line with the smaller O-N-O angle which we attribute to an interaction between hydrogen and remote oxygen.

The O-N-O angle is rather accurately determined since with any plausible set of the remaining parameters the rotational constants require values which do not differ by more than about  $2^\circ$  from those already given.

It is of interest to compare nitrous acid with two other substances which are isoelectronic with it and have nearly equal mass. These are formic acid and ONF. The former has an O-C-O angle of about  $125^\circ$ .<sup>7</sup> The latter presumably has an apex angle around  $116^\circ$ , considerably closer to that of nitrous acid. Unfortunately ONF has not been investigated by electron diffraction but a comparison of vibrational frequencies<sup>8,9</sup> shows that this molecule has a structure essentially identical with those of ONCl and ONBr. These molecules both have an apex angle of  $116^\circ$ <sup>10</sup> and have unusual internuclear distances which have been taken

TABLE IV. Probable values of the molecular parameters of HONO.

	<i>cis</i>	<i>trans</i>		
$r_{\text{HO}}$	0.98A <sup>a</sup>	0.98A <sup>a</sup>		
$r_{\text{ON}}$	1.46 <sup>b</sup>	1.46 <sup>c</sup>		
$r_{\text{NO}}$	1.20 <sup>a</sup>	1.20 <sup>a</sup>		
$\angle \text{HON}$	( $103^\circ$ )	( $105^\circ$ )		
$\angle \text{NON}$	114 <sup>ob</sup>	118 <sup>ob</sup>		
Estimated moments of inertia ( $\text{g cm}^2 \times 10^{10}$ )				
	HONO	DONO	HONO	DONO
$I_A$	10.13	12.1	7.83	8.21
$I_B$	68.4	69.6	75.2	80.8

<sup>a</sup> Estimated with assistance of frequency and force constant comparison.

<sup>b</sup> Calculated from rotational constants with use of remaining parameters.

<sup>c</sup> Assumed to be same as in *cis*-form.

<sup>7</sup> Van Zandt Williams, J. Chem. Phys. 15, 232 (1947).

<sup>8</sup> W. G. Burns and H. J. Bernstein, J. Chem. Phys. 18, 1669 (1950).

<sup>9</sup> E. A. Jones and P. J. H. Woltz, J. Chem. Phys. 18, 1516 (1950).

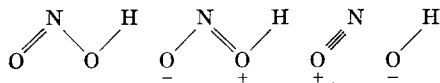
<sup>10</sup> J. A. Ketelaar and K. J. Palmer, J. Am. Chem. Soc. 59, 2629 (1937).

to indicate the contribution of an ionic structure to the ground state.

The higher NO frequency of nitrous acid ( $1696\text{ cm}^{-1}$ ) is, however, considerably lower than the corresponding frequency of ONF ( $1844\text{ cm}^{-1}$ ) which suggests that the short NO distance is considerably longer than the  $1.14\text{ \AA}$  found in the nitrosyl compounds. A comparison of the force constant with those of  $\text{N}_2\text{O}$  and  $\text{NO}_2$  leads to the conclusion that it is not greatly different from that found in those molecules, namely  $1.20 \pm 0.01\text{ A}$ , which is close to a double bond N—O distance.

The lower NO frequency of nitrous acid ( $\nu_4(\text{trans}) = 794\text{ cm}^{-1}$ ,  $\nu_4(\text{cis}) = 856\text{ cm}^{-1}$ ) lies between the NF valence frequency of ONF ( $767\text{ cm}^{-1}$ ) and that of  $\text{NF}_3$  ( $\nu_1 = 908\text{ cm}^{-1}$ ). The longer N—O distance in HONO is consequently bracketed by the  $1.37\text{ \AA}$ <sup>11</sup> found in  $\text{NF}_3$ , and the rather long N—F distance presumed to exist in ONF. It is fixed within rather close limits by the change of rotational constant with deuterium substitution which we believe shows that it is certainly not less and probably slightly greater than a normal N—O single bond distance.

From the foregoing it seems probable that the following three structures contribute significantly to the ground state of nitrous acid, though we are not in a position at present to estimate precisely their relative importance.



The last of these we presume to be responsible for the greater stability of the *trans*-isomer, which would be difficult to account for on the basis of the first two structures. From the O—N—O angle and the N—O frequency we conclude that the contribution of this structure is less than in the nitrosyl halides, although its effect is nevertheless extremely significant. The relative contributions of the second and third structures are presumably rather dependent on the O—N—O angle. As this angle changes in the bending vibration an unusually large change in charge distribution would consequently be expected. We suggest that this effect is responsible both for the "parallel" character of the  $598\text{ cm}^{-1}$  fundamental and for its high intensity as compared with the very weak bending fundamental of  $\text{NO}_2$ .

Since the third structure stabilizes the *trans*-

<sup>11</sup> V. Schomaker and C. S. Lu, J. Am. Chem. Soc. **72**, 1182 (1950).

tautomer one might reasonably expect its contribution to be greater to this form. This is indeed supported by the fact that in the *trans*-tautomer the low NO frequency is slightly lower and the high frequency higher than in the *cis*-form. The smaller O—N—O angle of the *cis*-form is probably not in contradiction to this belief but presumably results from an interaction between hydrogen and extreme oxygen indicated by the lower O—H valence frequency of the *cis*-form.

As points of dissimilarity between nitrous and formic acid we mention that the latter substance does not exist in a *trans*-form under circumstances so far investigated and does associate at pressures at which no indication of nitrous acid dimers was found.

#### THERMODYNAMIC AND OTHER PROPERTIES OF NITROUS ACID

Although the energy of the *trans*-form of nitrous acid is lower than that of the *cis*-form by about 506 calories, the torsional frequency of the *trans*-form is considerably the lower. Consequently it is evident that if the torsional potential is represented by a sum of cosine terms, at least three terms are required to fit the facts. The data available probably do not warrant an attempt to evaluate this function exactly, but we estimate that it has maxima of the order of  $12\text{ kcal mole}^{-1}$  above the lower minimum, at approximately  $\pm 88^\circ$  from the *trans*-position. This potential barrier is sufficiently large that one may question whether equilibrium was fully established in the studies of the rate of formation of nitrous acid by Wayne and Yost.<sup>2</sup> On the other hand, it is not so large that there can be much doubt that equilibrium was established in our measurements of the effect of temperature on relative intensities.

From the frequencies and moments of inertia given above we estimate for the standard molal entropies at  $25^\circ\text{C}$ :  $\bar{S}(\text{trans}) = 54.9\text{ e.u.}$  and  $\bar{S}(\text{cis}) = 54.8\text{ e.u.}$  From  $\Delta S$  and  $\Delta E$  we estimate for the equilibrium between the two forms:  $K_{25^\circ} = p_{\text{trans}}/p_{\text{cis}} = 2.5$ . This corresponds roughly to the average ratio of intensities of *trans*- and *cis*-bands. The standard entropy of the equilibrium mixture of nitrous acid is consequently  $56.0\text{ eu per mole at } 25^\circ$ .

#### ACKNOWLEDGMENT

The authors are greatly indebted to Dr. Oliver R. Wulf who suggested this investigation and gave very helpful advice, and to Dr. Verner Schomaker for discussions regarding structural problems.