

tion, would have a larger dipole moment than II'. It, therefore, should be associated to a greater extent and be favored in more polar solvents. Except for the anomaly in the 5% CS₂ solution, the chemical shifts tend to lower field as the solvent polarity increases. The greater change in $W(1)$ can be attributed to either a predominance of intermolecular hydrogen bonding to this proton or greater electron withdrawal from this bond by the carbonyl group in I'.

The solvent effects on the coupling constants also follow in that 3J_s should increase with an increase in I'. The decrease in the geminal HH coupling in highly polar solvents can be attributed to the increased electron-withdrawing ability of the carbonyl group in I', which should tend to make J_{gem} more negative.³⁵ Similar solvent effects on geminal coupling constants have been reported by Shapiro, *et al.*,³⁶ in formaldoximes.

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It is difficult to evaluate to what extent association plays an important part in the chemical shift variations since they and 3J_s are both solvent and temperature dependent. A plot of any chemical shift *vs.* 3J_s as a function of solvent or temperature is essentially linear although the slope of the plots differ considerably. It is found that solvent changes have greater effect on the chemical shifts (relative to 3J_s) than do temperature changes.

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The Microwave Spectrum, Structure, Dipole Moment, and Quadrupole Coupling Constants of *trans*-Nitrous Acid^{1a}

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Contribution from the Department of Physical Chemistry, The University, Bristol 8, England, and the National Bureau of Standards, Washington, D. C. Received July 18, 1966

Abstract: Mixtures of NO, NO₂, and H₂O in a wave guide cell have produced pressures of nitrous acid sufficient for the assignment of the *trans* isomer by microwave spectroscopy. Accurate values of the *B* and *C* ground-state rotational constants have been determined for the normal, deuterated, and nitrogen-15 species of *trans*-nitrous acid. The data are consistent with the expected planar configuration and on this basis the following structure has been calculated for *trans*-nitrous acid: N—O(H) = 1.433, N=O = 1.177, and O—H = 0.954 Å; ∠ONO = 110° 39' and ∠NOH = 102° 3'. Quadrupole coupling constants for the nitrogen-14 nucleus in the normal and deuterated species have been determined; the values for *trans* HNO₂ are: $\chi_{aa} = 1.91$, $\chi_{bb} = -5.39$, and $\chi_{cc} = 3.48$ Mc/sec. The components of the dipole moment in the nitrogen-15 molecule have been determined to be $\mu_a = 1.387 \pm 0.01$ and $\mu_b = 1.223 \pm 0.06$ D., and yield a value for the total dipole moment of 1.85 ± 0.06 D., inclined at an angle of $41^\circ 24' \pm 24'$ to the *a* principal axis. The structure of *trans*-nitrous acid is discussed on the basis of these data.

Nitrous acid cannot be obtained in the pure state and as a result rather little has been determined about its accurate molecular structure. Its chemical reactions in aqueous solution are very well known,^{2a} but it is only comparatively recently that the existence of nitrous acid as a gaseous species has been firmly established, mainly on the basis of the infrared^{2b,3a} and ultraviolet⁴ spectra. Detailed vibrational analyses

of the infrared spectrum³ have shown the molecule to occur in comparable amounts of *cis* and *trans* tautomeric forms, with the *trans* form being lower in energy by about 530 cal/mole. The potential barrier restricting internal rotation of the OH group for the *cis* form was found to be about 10.8 kcal/mole.^{3b} In the matrix at 20°K this barrier has been estimated as 9.7 ± 0.7 kcal/mole.⁵

In the gas phase nitrous acid can be studied only in the presence of its dissociation products NO, NO₂, and water vapor, together with N₂O₄, N₂O₃, and nitric acid. The various equilibria concerned have been studied by a number of authors.⁶ The available data indicate that at room temperature and at a pressure of

(1) (a) The results of this research were presented in part at the Ohio State Symposium on Molecular Structure and Spectroscopy, June 1965; (b) The University, Bristol; (c) National Bureau of Standards; NRC-NBS Postdoctoral Research Associate 1964-1966. Present address: Department of Chemistry, University of Michigan, Ann Arbor, Mich.

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Table I. Microwave Spectrum of *trans*-Nitrous Acid and Isotopic Species

Transition		HONO,	Δ^a	DONO,	Δ	HON ¹⁸ O,	Δ
$J'-J$	$F'-F$	obsd ^b		obsd ^b		obsd ^d	
1 ₀₁ -0 ₀₀	2-1	23,541.51	-0.03	21,971.11	0.00	23,473.57	0.00
	0-1	23,540.61 ^c	0.02	21,970.35 ^c	0.00		
	1-1	23,542.04	0.02	21,971.61	0.00		
2 ₀₂ -1 ₀₁		47,061.75 ^d	0.00	43,924.26 ^e	0.00		
2 ₁₂ -1 ₁₁		45,574.86 ^d	0.12	42,578.31 ^e	0.44		
2 ₁₁ -1 ₁₀				45,304.93 ^e	0.60		
4 ₁₃ -4 ₁₄	3-3	15,074.86	-0.03	13,630.05 ^d	0.00	15,641.71	0.03
	5-5	15,075.59	0.01	13,630.80 ^d	0.01		
	4-4	15,078.63	0.00	13,633.76 ^d	0.00		
5 ₁₄ -5 ₁₅	4-4	22,608.70	-0.03	20,442.45 ^d	0.05	23,457.41	-0.03
	6-6	22,609.33	0.01	20,443.11 ^d	0.00		
	5-5	22,612.41	-0.01	20,446.14 ^d	-0.04		
6 ₁₅ -6 ₁₆	5-5	31,642.61	0.00	28,612.14	0.01	32,828.17	0.00
	7-7	31,643.14	-0.01	28,612.65	0.01		
	6-6	31,646.21	0.03	28,615.71	-0.02		

^a Δ = calculated frequency - observed frequency. ^b Accuracy ± 0.1 Mc/sec. ^c Accuracy ± 0.15 Mc/sec. ^d Accuracy ± 0.2 Mc/sec. ^e Accuracy ± 0.3 Mc/sec.

1 atm only about 10% nitrous acid is obtainable. At the low pressures (about 0.1 torr) necessary to study the microwave spectrum, the most nitrous acid obtainable is about 0.3% at room temperature.

With this information at hand the microwave investigation was begun in an effort to obtain detailed information about the molecular structure of *cis*- and *trans*-nitrous acid. A comparison of the structural parameters in *cis*- and *trans*-nitrous acid should give a measure of the effect of nonbonded interactions on the bond distances and angles in the system. We are able to report here the microwave assignment and molecular structure, dipole moment, and quadrupole coupling constants of *trans*-nitrous acid, the *cis* isomer as yet being unassigned.

Experimental Section

Mixtures of NO, NO₂, and water vapor were dosed into a conventional Stark modulated microwave absorption cell and pumped down to operating pressures of approximately 0.1 torr. A search was begun throughout the region 22-25 Gc/sec where the 1₀₁-0₀₀ transitions of both *cis*- and *trans*-nitrous acid were expected to occur on the basis of reasonable molecular models. One good absorption candidate was located at 23,540 Mc/sec, having a typical 0 \rightarrow 1 Stark effect, which at lower pressures resolved into a triplet characteristic of nitrogen quadrupole coupling for a 0 \rightarrow 1 transition. It was strongly indicated that this absorption was due to nitrous acid since mixtures of the three reactants, NO, NO₂, and H₂O were necessary to produce the transition. The assignment of this line as a 1₀₁-0₀₀ transition was confirmed by measurements at higher frequencies of the 2₀₂-1₀₁ transition at 47,062 Mc/sec and the 2₁₂-1₁₁ transition at 45,575 Mc/sec. On the basis of these three lines a series of $K_{-1} = 1$, μ_a Q-branch transitions were predicted and measured. Subsequent assignment of the deuterated species showed the assigned spectra to be due to the *trans* species of nitrous acid.

The observed intensities were rather weak and were optimized by dosing the absorption cell from separate bulbs of NO, NO₂, and water vapor. The spectra were observed at both Dry Ice and room temperatures with little change in peak intensities. Although the rotational lines studied are basically stronger at Dry Ice temperatures, the concentration of nitrous acid in the absorption cell is limited by the presence of condensed phase-vapor equilibria at low temperatures. Both the observed weak intensities as well as the pressure and temperature dependence of the intensities agreed with calculations based on the equilibria data which further confirmed the assignment to nitrous acid.

The observed frequencies given in Table I were measured in Stark spectrometers modulated at 100 and 80 kc/sec. Measurements were made on the normal, deuterated, and nitrogen-15 species of *trans*-nitrous acid. HN¹⁵O₂ was prepared by mixing H₂O and N¹⁴O₂, along with NO enriched to 97% in N¹⁵O.

Spectral Analysis and Rotational Constants

Several of the transitions were resolvably split by interaction of the nitrogen-14 quadrupole moment with the over-all rotation. These transitions were analyzed to give the unperturbed transition frequencies and quadrupole coupling constants using the asymmetric rotor theory of Bragg and Golden.⁷

The unperturbed centers of the $K_{-1} = 1$, μ_a Q-branch lines were analyzed for $B - C$ and the centrifugal distortion constant δ_J using the first-order centrifugal distortion treatment of Kivelson and Wilson.⁸ Expansions in the asymmetry parameter $\delta = (B - C)/(A - C)$ were used in solving for the rigid part of the frequencies and led to the following equations.⁹

$$4_{13}-4_{14} = 10(B-C) - 2.461(B-C)\delta^2 - 800\delta_J$$

$$5_{14}-5_{15} = 15(B-C) - 9.845(B-C)\delta^2 - 1800\delta_J$$

$$6_{15}-6_{16} = 21(B-C) - 29.531(B-C)\delta^2 - 3528\delta_J$$

This value of $B - C$ was combined with the 1₀₁-0₀₀ transition frequency to obtain the B and C rotational constants. The A rotational constant has been calculated from the 2₀₂-1₀₁ transition, again using the δ expansion for the rigid rotor frequency. A symmetric top correction for centrifugal distortion, amounting to 0.24 Mc/sec has been made by assuming $D_J = 0.01$ Mc/sec, close to that found for formic acid.¹⁰

Similar procedures were adopted for DNO₂ and HN¹⁵O₂, except no attempt was made to obtain the A constant for the latter species. The observed and calculated spectra are given in Table I. The rotational constants are given in Table II along with the other molecular constants.

Dipole Moment

Stark effect coefficients were measured for the $M = 0$, 1₀₁-0₀₀ transition and for the $M = 4$ and 5 components of the 5₁₄-5₁₅ transition. The measurements were made on the nitrogen-15 species to obtain sharper lines free from quadrupole effects. The Stark displacements were compared with those of the OCS molecule for

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(10) G. Erlandsson, *ibid.*, **28**, 71 (1958).

Table II. Spectroscopic Constants (Mc/sec) and Moments of Inertia^a (amu A²) of *trans*-Nitrous Acid and Isotopic Species

Constants	HONO	DONO	HON ¹⁸ O	Accuracy
<i>A</i>	92,500	88,900		±1700
<i>B</i>	12,524.78	11,667.31	12,519.04	±0.05
<i>C</i>	11,016.84	10,303.92	10,954.53	±0.05
$\delta_J \times 10^3$	2.2	1.7	2.3	±0.3
<i>X</i> _{aa}	1.91	1.68		±0.12
<i>X</i> _{bb}	-5.39	-5.17		±0.30
<i>X</i> _{cc}	3.48	3.49		±0.18
<i>I</i> _a	5.46	5.68		±0.12
<i>I</i> _b	40.3625	43.3289	40.3810	±0.0002
<i>I</i> _c	45.8871	49.0621	46.1481	±0.0002
$\Delta = I_c - I_b - I_a$	0.06	0.05		±0.12

^a Conversion factor $BI = 505,531$ (Mc/sec) amu A².

which the dipole moment was taken to be 0.7124 D.¹¹ The observed and calculated Stark coefficients are given in Table III. μ_a was determined to be 1.387 ± 0.01 D. and μ_b to be 1.223 ± 0.06 D. These give a value for the total dipole moment of 1.85 ± 0.06 D. directed at $41^\circ 24' \pm 24'$ to the *a* principal axis.

Table III. Stark Coefficients and Dipole Moment of *trans*-HON¹⁸O

Transition	$-\Delta v/E^2$ (Mc/sec)/(v/cm) ² × 10 ⁶	
	Observed	Calculated
$1_{01}-0_{00} M=0$	11.75 ± 0.10	11.72
$5_{14}-5_{15} M=4$	2.00 ± 0.15	1.94
$M=5$	2.92 ± 0.15	2.92
$\mu_a = 1.387 \pm 0.01$; $\mu_b = 1.223 \pm 0.06$		
$\mu = 1.85 \pm 0.06$		

The orientation of the dipole moment relative to the molecular framework was not uniquely determined. Two possibilities exist: (a) μ_T inclined $71^\circ 38'$ to the central N-O (H) bond; (b) μ_T inclined $11^\circ 10'$ to the central N-O (H) bond. From a consideration of the likely charge distribution, the authors prefer orientation a. This is illustrated in Figure 1.

Molecular Structure

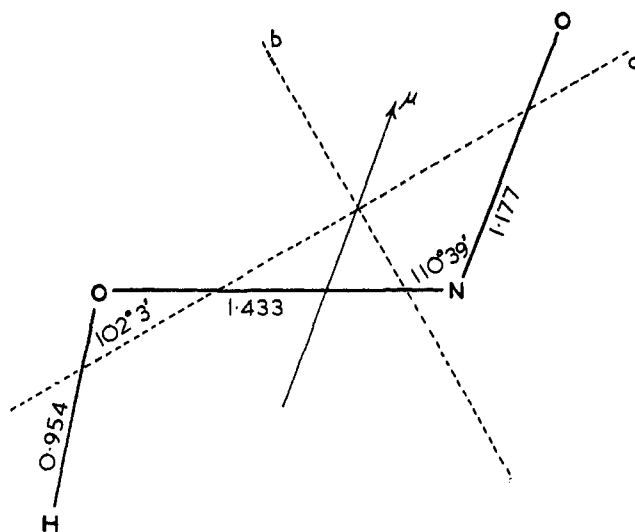
The microwave data are strongly indicative of the expected planar configuration, and the structural calculations have been carried out on this basis.

The *a* and *b* coordinates of the hydrogen atom in the principal axis system of HNO₂ were calculated using Kraitchman's equations for a planar molecule.¹² $I_c^0 - I_b^0$ and I_b^0 were used for the HNO₂-DNO₂ data to yield the following values: $|a| = 1.7298$ and $|b| = 0.4792$ A. The small value for the *b* coordinate is only compatible with the assignment of the spectrum to the *trans* isomer of nitrous acid. On the basis of a series of reasonable structures fitting $I_c^0 - I_b^0$ and I_b^0 of HNO₂, the frequency shift in the $1_{01}-0_{00}$ transition on deuteration was calculated to be 1594 Mc/sec with the hydrogen in the *trans* position and 666 Mc/sec for a *cis* structure. The observed isotopic shift was found to be 1571 Mc/sec showing conclusively that the hydrogen atom in this species was in fact *trans*.

The *a* and *b* coordinates of the nitrogen atom were also calculated, using Kraitchman's equations, to

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Figure 1. Structure of *trans*-nitrous acid.

have the values: $|a| = 0.1369$ and $|b| = 0.4984$ A. The remainder of the structure was solved using the equations

$$I_b^0 = \sum_i m_i a_i^2; \quad \sum_i m_i a_i = \sum_i m_i b_i = \sum_i m_i a_i b_i = 0$$

The structure thus obtained is given in column I of Table IV. However, it is estimated on the basis of

Table IV. Structural Parameters in *trans*-HNO₂^a

	I	II
O-H, A	0.959	0.954
NOH	$101^\circ 38'$	$102^\circ 3'$
ONO	$110^\circ 58'$	$110^\circ 39'$
N-O, A	1.420	1.433
N=O, A	1.190	1.177

^a The different procedures used to obtain the parameters in columns I and II (and the reason for considering those in column II the preferred set) are discussed in the text. In column II, the bond distances are expected to be accurate to ± 0.01 A and the angles to $\pm 30'$, for comparison with substitution structures.

several known cases that the small *a* coordinate of the nitrogen atom calculated by this procedure will be underestimated by about 0.01 A owing to changes in the effective structural parameters with isotopic substitution.¹³ Close examination of the small carbon or nitrogen coordinates, similar in magnitude to a_N in the present case but where an alternative method of calculation is available, in CF₂O,¹⁴ CH₂N₂,¹⁵ CH₂NOH,¹⁶ N₂O,¹⁷ CFHO,¹⁸ and HNO₃,¹⁹ show an underestimation of between 0.011 and 0.017 A in the small coordinate. Disregarding changes in the ONO bond angle, effects of this magnitude in HNO₂ could be attributed to a shortening of 6×10^{-5} A in each of the NO bonds on substitution with nitrogen-15 and

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(18) O. H. Le Blanc, Jr., V. W. Laurie, and W. D. Gwinn, *ibid.*, **33**, 598 (1960).

(19) A. P. Cox and J. M. Riveros, *ibid.*, **42**, 3106 (1965).

lead to a reestimate of the nitrogen coordinates: $|a| = 0.1497$ and $|b| = 0.4989$ Å. The oxygen coordinates are now calculated as before using the hydrogen coordinates obtained previously. The structure is given in column II of Table IV and in Figure 1, and is considered the best structure obtainable from the present data. The NOH and ONO bond angles are little affected by this correction procedure, but the NO bonds are changed by about 0.01 Å and this difference is a useful guide to the accuracy which can be placed on the bond distances in *trans*-nitrous acid. It should be pointed out that these structural parameters for *trans*-nitrous acid differ significantly from the earlier estimate^{3a} obtained from infrared frequency and force constant comparisons and a rough estimate of $A - \frac{1}{2}(B + C)$.

Discussion

Before discussing the structural parameters, the evidence for assigning the observed spectrum to *trans*-nitrous acid will be summarized.

(1) Only mixtures of NO, NO₂, and H₂O yield the observed spectrum; any two components are not sufficient.²⁰ The observed intensities of the transitions as well as the pressure and temperature dependence of the intensities agreed with calculations based on the known equilibria data for nitrous acid.

(2) The deuterium data show the molecule to possess a *trans*-hydrogen atom.

(3) The nitrogen-14 quadrupole coupling data show the presence of a single nitrogen nucleus, which on the basis of the small nitrogen-15 isotopic shift must be close to both principal axes, *i.e.*, close to the center of mass of the molecule.

(4) Structural fitting of the experimental moments of inertia leads to the only reasonable conclusion that the observed species is *trans*-nitrous acid.

The structural parameters of *trans*-nitrous acid can be usefully compared with those of several other molecules but particularly nitric acid¹⁹ and formaldoxime.¹⁶ For example, the OH bond distance (0.954 Å) and the NOH bond angle (102° 3') compare closely with those obtained in nitric acid (0.964 Å, and 102° 9') and formaldoxime (0.956 Å and 102° 41'). The ONO angle of 110° 39' is very close to that in formaldoxime (110° 12') and also the value of 110° 12' obtained in nitrosyl fluoride,²¹ but is considerably smaller than the

(20) Interestingly enough the 1₀₁-0₀₀ transition of *trans*-nitrous acid was observed independently in microwave spectral studies of the N₂O₈-HNO₃ system. The nitric acid lines steadily lost intensity owing to reaction within the copper wave guide cell, and stable lines, later shown to be those of *trans*-nitrous acid, grew in.

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corresponding angle in nitric acid (113° 51') and the value of 115.4° obtained in the nitrite ion.²²

The ONO angle in nitrous acid may be taken to indicate about 26% s hybridization in the NO σ bonds. If we adopt this value for the most probable resonance contributor HO—N=O together with a value of $q_{210} = -10$ Mc/sec for nitrogen,²³ values of $\chi_{aa} = 2.6$, $\chi_{bb} = -5.2$, and $\chi_{cc} = 2.6$ Mc/sec may be calculated for the quadrupole coupling constants.²⁴ Thus the normal valence structure of the molecule gives a useful fit to the observed coupling constants. The calculation does not rule out possible contributions from structures such as HO⁺=N—O⁻ and H⁺O⁻—N=O. However, the inclusion of other structures such as HO⁻N≡O⁺ and HO⁻N⁺=O, which might be expected to contribute to the final hybrid, do not improve the moderate fit to the out-of-plane coupling constant χ_{cc} (observed 3.5 Mc/sec).

Moreover, the determined NO bond distances themselves do not give much indication of large contributions from structures other than the O—N=O type. The central NO bond distance of 1.433 Å is only slightly shorter than the 1.44 Å usually quoted for a pure NO single bond, while the N=O bond distance of 1.177 Å is only about 0.01 Å shorter than the 1.19 Å expected for a pure NO double bond. In formaldoxime and nitric acid, however, the central NO bond is somewhat shorter at 1.407 Å, and this shortening has been attributed to double bond character to the extent of conferring planarity on these molecules and in contributing at least in part to the extremely high barrier to rotation about this bond. Nitrous acid is also planar with a high internal barrier (10.8 kcal/mole), despite having an essentially single central bond, and this fact would seem to conflict with the usual correlation of bond order *vs.* barrier to rotation. It has been suggested,⁵ therefore, that the barrier may be associated with repulsion between the nonbonding electrons of the nitrite group. While these interactions are expected to be important, it seems unlikely that the high barrier and relative stability of the isomers of nitrous acid (and the same properties for related compounds such as formaldoxime, nitric acid, and formic acid) can be simply explained in terms of this type of interaction alone.

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