307. *The Microwave Spectrum of Nitric Acid.*

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The rotational spectra of HNO_3, DNO_3, and $H^{15}NO_3$ have been analysed and the moments of inertia of these three isotopic species determined. Thence the distance between the oxygen atoms of the nitro-group has been determined as 2·190 ± 0·003 Å. The perpendicular distance of the third oxygen atom from the line joining the two oxygen atoms of the nitro-group is 1·912 ± 0·003 Å. With r_0(O–H) assumed to be 0·96 Å, the following structural parameters were calculated with the aid of the five moment equations: r_0(N–OH) = 1·405 ± 0·005 Å, r_0(N–O) = 1·206 ± 0·005 Å, ∠ONO = 130° ± 20′, ∠NOH = 102° ± 30′.

The value of the dipole moment of HNO_3 determined from the Stark effect of the two $J = 1 \longleftarrow 0$ transition was 2·16 ± 0·04D.

Nitrogen nuclear quadrupole coupling coefficients are reported for HNO_3 and DNO_3.

PREVIOUS attempts to determine the structure of the nitric acid molecule in the vapour phase have involved the use of electron-diffraction [1] and infrared and Raman techniques.[2]

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[1] Maxwell and Moseley, *J. Chem. Phys.*, 1940, **8**, 742.

[2] Ingold, Cohn, and Poole, *J.*, 1952, 4272; Ingold and Millen, *J.*, 1950, 2612.

Maxwell and Moseley,[1] on the basis of their electron-diffraction results, inferred a planar structure with r(N–OH) = 1·41 ± 0·02 Å, r(N–O) = 1·22 ± 0·02 Å, and $\angle$ONO = 130° ± 5°. The hydrogen atom was not located, and its position was assumed. Ingold, Cohn, and Poole [2] gave reasons for preferring 135° for the angle in the NO_2 group ($\angle O_ANO_B$).

The present investigation has confirmed the planarity of the molecule on the basis of inertial defect considerations.[3] The co-ordinates of the hydrogen atom have been accurately determined from the increases in the moments of inertia on deuteration. The relative positions of the oxygen atoms have also been obtained and it is shown that a small perturbation of the C_{2v} symmetry of the NO_3 group is present. The co-ordinates of the heavy atoms have also been determined by solving the ground-state moment equations.

The Spectrum.—The pure rotational spectra of HNO_3, DNO_3, and $H^{15}NO_3$ were investigated in the region 8000—35,000 Mc./sec. Assignments were made on the basis of

TABLE 1.

(*a*) *The rotational spectrum of* HNO_3 *and* DNO_3 (*Mc./sec.*).

R-*Branch*			Q-*Branch*		
Trans.	HNO_3	DNO_3	Trans.	HNO_3	DNO_3
$1_{01} \leftarrow 0_{00}$ ($F = 0 \leftarrow 1$)	18360·06	17347·27	$2_{11} \leftarrow 2_{12}$	17517·51	15832·83
($F = 2 \leftarrow 1$)	18360·48	17347·64	$3_{21} \leftarrow 3_{22}$	16215·59	13579·09
($F = 1 \leftarrow 1$)	18360·78	17347·89	$4_{31} \leftarrow 4_{32}$	14534·25	10807·99
$1_{11} \leftarrow 0_{00}$ ($F = 1 \leftarrow 1$)	19271·45	19005·40	$5_{41} \leftarrow 5_{42}$	12540·98	7833·96
($F = 2 \leftarrow 1$)	19271·69	19005·61	$6_{51} \leftarrow 6_{52}$	10344·23	—
($F = 0 \leftarrow 1$)	19272·06	19005·89	$7_{61} \leftarrow 7_{62}$	8097·58	—
$2_{12} \leftarrow 1_{11}$ ($F = 1 \leftarrow 0$)	30881·24	29417·40	$3_{12} \leftarrow 3_{13}$	—	29138·41
($F = 3 \leftarrow 2$)	30881·69		$4_{22} \leftarrow 4_{23}$	—	27215·84
($F = 2 \leftarrow 1$)	30881·92		$5_{32} \leftarrow 5_{33}$	29175·32	24229·63
$2_{12} \leftarrow 1_{01}$ (unres.)	31792·80	31075·40	$6_{42} \leftarrow 6_{43}$	27369·67	20396·03
			$7_{52} \leftarrow 7_{53}$	24993·51	16065·29

Q-*Branch* (contd.)

Trans.	HNO_3	DNO_3	Trans.	HNO_3	DNO_3
$8_{62} \leftarrow 8_{63}$	22147·00	11680·10	$8_{53} \leftarrow 8_{54}$	—	32137·90
$9_{72} \leftarrow 9_{73}$	18969·56	—	$9_{63} \leftarrow 9_{64}$	—	26938·68
$10_{82} \leftarrow 10_{83}$	15628·19	—	$10_{73} \leftarrow 10_{74}$	—	21229·43
$11_{92} \leftarrow 11_{93}$	12317·35	—	$11_{83} \leftarrow 11_{84}$	—	15553·69
$12_{10,2} \leftarrow 12_{10,3}$	9245·56	—	$12_{93} \leftarrow 12_{94}$	—	10487·08

(*b*) *The rotational spectrum of* $H^{15}NO_3$ (*Mc./sec.*)

Trans.	$1_{01} \leftarrow 0_{00}$	$1_{11} \leftarrow 0_{00}$	$2_{12} \leftarrow 1_{11}$	$2_{12} \leftarrow 1_{01}$
Frequency	18357·05	19272·44	30877·22	31792·60

the Stark effect, with the aid of Q-branch diagrams. The frequencies of the assigned rotational lines of the three isotopic species are listed in Table 1. The quadrupole interaction of the ^{14}N nucleus caused a very small splitting of the spectral lines of HNO_3 and DNO_3. The hyperfine structure of certain low-J transitions of these molecules was resolved by cooling both the absorption cell and the sample to −78° where the vapour pressure of nitric acid is less than 5 × 10^{-3} mm. Hg, and the line-width was narrow enough to resolve the hyperfine components. By using the formulation of Bragg and Golden [4] the quadrupole coupling coefficients of HNO_3 and DNO_3 were determined from the hyperfine structure of the $1_{01} \leftarrow 0_{00}$ and $1_{11} \leftarrow 0_{00}$ transition of these molecules. The coefficients may be designated eQq_{aa}, eQq_{bb}, and eQq_{cc}, where e is the proton charge, Q the quadrupole moment of the nucleus, and q_{aa}, q_{bb}, and q_{cc} the electric field gradients at the nitrogen nucleus along the a-, b-, and c-axes of the molecule respectively. The values of the coupling coefficients obtained from the $J = 1 \leftarrow 0$ transitions are listed in Table 2. They were confirmed (for HNO_3) by comparison of the observed and the calculated hyperfine structure of the transition $2_{12} \leftarrow 1_{11}$. The eQq_{cc}'s are very small, and may not be different from zero when the experimental error is taken into account.

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[3] Millen and Morton, *Chem. and Ind.*, 1956, 954.

[4] Bragg and Golden, *Phys. Rev.*, 1949, **75**, 735.

This implies that the field gradient at the nitrogen nucleus along an axis perpendicular to the molecular plane is very small.

TABLE 2. *Ground-state rotational constants, moments of inertia, and nuclear quadrupole coupling constants of nitric acid.*

	HNO_3	DNO_3	$H^{15}NO_3$		HNO_3	DNO_3	$H^{15}NO_3$
A_0 (Mc./sec.) ...	13011·15	12970·71	13012·35	$I_A°$ (amu Å²) ...	38·85368	38·97481	38·85008
B_0	12099·93	11312·82	12096·97	$I_B°$	41·77966	44·68656	41·78990
C_0	6260·60	6034·86	6260·09	$I_C°$	80·74801	83·76847	80·75465
κ	$0·73003_1$	$0·52192_0$	$0·72886_4$	Δ (amu Å²) ...	0·11467	0·10710	0·11467

	HNO_3	DNO_3
eQq_{aa} (Mc./sec.)	$+0·93 \pm 0·05$	$+0·82 \pm 0·05$
eQq_{bb} ,,	$-0·82 \pm 0·05$	$-0·62 \pm 0·05$
eQq_{cc} ,,	$-0·11 \pm 0·10$	$-0·20 \pm 0·10$

Included in Table 2 are the ground-state rotational constants A_0, B_0, and C_0 of HNO_3, DNO_3, and $H^{15}NO_3$. They were determined from the frequencies of the transitions $1_{01} \longleftarrow 0_{00}$, $1_{11} \longleftarrow 0_{00}$, and $2_{12} \longleftarrow 1_{11}$. For HNO_3 and DNO_3 the " unperturbed " frequencies of the transitions were calculated from the spectrum and used to determine the rotational constants. For $H^{15}NO_3$, of course, quadrupole effects were absent. The rotational constants given in Table 2 reproduced the observed spectra within ±1·5 Mc./sec. up to $J = 5$. The higher-J Q-branch transitions, however, were shifted from their calculated positions by up to 10 Mc./sec. owing to centrifugal distortion. Chiefly because of the asymmetry of the molecule, no satisfactory way of applying a correction for centrifugal distortion could be devised. Table 2 also includes the ground-state moments of inertia of the three isotopic species. From these were calculated the inertial defects $\Delta = I_C° - I_B° - I_A°$. The planarity of the molecule may be inferred from the magnitude and sign of Δ. Positive inertial defects of the order of 0·1 amu Å² are expected from the ground-state moments of inertia of planar molecules. It is interesting that Δ was unaffected by replacement of ^{14}N by ^{15}N, but decreased appreciably on deuteration.

Determination of the Molecular Structure.—The microwave spectrum of the nitric acid molecule yielded no evidence of internal motion; it was consistent with a very high barrier to O–H torsion. Ingold, Cohn, and Poole[2] estimated a barrier height of 10 kcal./mole against this motion. Our conclusions regarding the geometry of the molecule are based on the assumption of a rigid planar model.

The co-ordinates of the hydrogen atom in the inertial axis system (a–b plane) of HNO_3 were determined with the aid of Kraitchman's equations,[5] which relate the changes in the moments of inertia on isotopic substitution to the co-ordinates of the atom replaced. Applying the same procedure to the determination of the nitrogen co-ordinates gives an imaginary value for the distance of the nitrogen atom from the a-axis (b_s), since $I_A°$ had decreased on replacement by the heavier atom (see Table 2). This was attributed to the fact that the nitrogen atom is close to the centre of mass, and is particularly close to the a-axis. For the ^{14}N species we may write

$$A_0 = A_e - \sum_i \alpha_i d_i/2 = A_e - \bar{\alpha}$$

where A_0 and A_e are the ground-state and equilibrium rotational constants respectively. Similarly for the ^{15}N species, we have:

$$A_0' = A_e' - \bar{\alpha}'$$

The right-hand side of the equation

$$A_0 - A_0' = (A_e - A_e') - (\bar{\alpha} - \bar{\alpha}')$$

is the difference between two positive terms. On substitution very close to the a-axis,

[5] Kraitchman, *Amer. J. Phys.*, 1953, **21**, 17.

the change in A_e may be less than that in $\bar{\alpha}$, causing an apparent increase in A_0 on replacement by the heavier atom. Consequently, it can only be concluded from the observed ΔI_A° that the nitrogen atom lies on or very close to the *a*-axis.

Having determined the co-ordinates of the hydrogen atom in the inertial axis system of HNO_3, we calculated the moments of inertia of the NO_3 group with the aid of Kraitchman's equations. A hypothetical isotope of mass zero was substituted for the hydrogen atom. The values obtained for $^{14}NO_3$ were $I_A^\circ = 37{\cdot}89016$ and $I_B^\circ = 39{\cdot}61195$ amu Å^2. A similar calculation for $^{15}NO_3$ gave $I_A^\circ = 37{\cdot}89189$ and $I_B^\circ = 39{\cdot}61578$ amu Å^2. These figures led immediately to an estimate of the co-ordinates of the nitrogen atom in the NO_3 axis system. Little reliability could, however, be placed on them as the nitrogen atom is so close to the centre of mass. The direction of the principal axes of $^{14}NO_3$ were also obtained from the position of the hydrogen atom in this framework. Two possibilities were apparent: one in which the *b*-axis coincided with $N\text{–}O_c$ (O_c being the oxygen atom to which the hydrogen is attached in HNO_3), and the other in which the *a*-axis was inclined at an angle 24—28° to $N\text{–}O_c$. The second alternative was favoured by a calculation of eQq's along and perpendicular to $N\text{–}O_c$, giving values almost equal in HNO_3 and DNO_3, and of the correct magnitude. This was not the case if the *b*-axis were assumed to lie along the bond $N\text{–}O_c$. The value of $r(O\text{–}H)$ assumed in the above calculations was $0{\cdot}95 \pm 0{\cdot}05$ Å, leading to an angle between $N\text{–}O_c$ and the *a*-axis of $26° \pm 2°$. Of course, this result implies a perturbation of the C_{2v} symmetry of the NO_3 group. The directions of the principal axes of NO_3 are very sensitive to slight perturbations of the C_{2v} symmetry of the group, and it was shown that a displacement of $N\text{–}O_c$ from the symmetrical position by less than 1° would account for the observed directions of the principal axes.

It was now possible to calculate certain parameters of the three oxygen atoms. The nitrogen atom is near enough to the centre of mass not to affect the results unless we wish to calculate actual bond lengths. The following figures were obtained: $O_AO_B = 2{\cdot}190 \pm 0{\cdot}003$ Å, and the perpendicular distance of O_c to O_AO_B was $1{\cdot}912 \pm 0{\cdot}003$ Å. The limits of error quoted here come directly from the assumption $r(O\text{–}H) = 0{\cdot}95 \pm 0{\cdot}05$ Å, and the distances have a status similar to that of the usual r_0 values. Since $r(O\text{–}H)$ is almost certainly within this range, the above interoxygen parameters lie equally certainly within the range specified. In Table 3 the values of O_AO_B in nitric acid are compared with figures calculated from data in certain other molecules. The agreement between the different sets of data is excellent. It appears that the interoxygen distances are the only parameters of the nitric acid molecule which may be specified with any certainty, since the position of the nitrogen atom cannot be accurately determined. However, by using the five moment equations, a complete structural determination was possible with the aid of certain assumptions regarding the position of the nitrogen atom.

TABLE 3. *Comparison of the bond lengths* (Å) *and dihedral angle of the nitro-group in certain compounds.*

Molecule	∠ONO	r(N–O)	O_A–O_B	Molecule	∠ONO	r(N–O)	O_A–O_B
NO_2Cl	130° 35′ ± 15′	1·202 ± 0·001	2·185	CH_3NO_2	130° (assumed)	1·204	2·182
HNO_3	130° ± 20′	1·206 ± 0·005	2·190	NO_2F	130° (assumed)	1·207	2·187

The position of the hydrogen atom in the HNO_3 axis system is accurately known. In terms of the distances along the *a*- and the *b*-axis its co-ordinates are (1·6771, 0·4937) Å. The nitrogen position is less well known, although it must lie close to the *a*-axis. In order to determine the molecular structure the nitrogen atom was first assumed to lie on the *a*-axis. The observed moments of inertia I_A° and I_B° of $H^{15}NO_3$ were increased by 0·00360 amu Å^2. This " correction " equalised the I_A° of $H^{14}NO_3$ and $H^{15}NO_3$, and was also applied to the I_B° since it was thought that zero-point effects would be equal in the two axes. By using Kraitchman's equations the approximate co-ordinates for the nitrogen in the HNO_3 axis system were then calculated. With the co-ordinates of the hydrogen and nitrogen atoms determined, their contributions were removed from the five in-plane moment equations, which thereafter involved only the six co-ordinates of the three oxygen atoms. One further assumption was made in order to provide the necessary sixth equation. It was assumed that $r(\text{O–H}) = 0{\cdot}96$ Å. This figure is close to the value for water,[6] and was expected to be within one-hundredth of an Ångström of the true value in nitric acid. Further, it was shown above that the positions of the heavy atoms are comparatively insensitive to small variations in $r(\text{O–H})$. The six oxygen co-ordinates were then calculated from these equations by an iterative method, using as a starting point the oxygen skeleton arrived at in the previous section. This was necessary because physically two structures may be obtained from the equations, one of which is chemically absurd. The three oxygen atoms lie almost on a circle centred at the centre of mass, and this circle is obviously intersected in two points by the circle defined by $r(\text{O}_\text{c}\text{–H}) = 0{\cdot}96$ Å. The configuration leading to an almost symmetrical structure for the nitro-group was chosen. The structure so obtained (with the nitrogen atom assumed to lie on the *a*-axis) had the two bonds N–O_A and N–O_B differing by 0·04 Å. Since there are chemical reasons for regarding the two bonds in a nitro-group as equivalent, the nitrogen atom was moved off the *a*-axis by ~0·02 Å in order to equate N–O_A and N–O_B. With this re-estimation of the nitrogen position, the six equations were again iterated to yield corrected oxygen co-ordinates. In order to remove the uncertainty in the nitrogen position it will be necessary to determine the moments of inertia of the three $\text{HNO}_2{}^{18}\text{O}$ species. With the three oxygen co-ordinates directly determined, the nitrogen position may be calculated from the first-moment equations.

The molecular parameters at which we arrived are summarized in Table 4 and the Fig. The interoxygen distances given are independent of assumptions regarding the nitrogen atom. The other molecular parameters depend for their validity on certain assumptions (which have been specified) regarding the position of the nitrogen atom. There is again evidence of a slight deviation from C_{2v} symmetry in the NO_3 group.

TABLE 4. *The structural parameters of* HNO_3.

$r_0(\text{O–H}) = 0{\cdot}96$ Å (assumed)
$r_0(\text{N–OH}) = 1{\cdot}405 \pm 0{\cdot}005$ Å
$r_0(\text{N–O}) = 1{\cdot}206 \pm 0{\cdot}005$ Å
$\angle\text{NO}_\text{C}\text{H} = 102° \pm 30'$
$\angle\text{O}_\text{A}\text{NO}_\text{B} = 130° \pm 20'$
$\angle\text{O}_\text{A}\text{NO}_\text{C} = 114° \pm 20'$
$\angle\text{O}_\text{B}\text{NO}_\text{C} = 116° \pm 20'$

It is interesting to compare the structure of the NO_2 ($\text{O}_\text{A}\text{NO}_\text{B}$) group in nitric acid with that of the same group in other molecules. In nitric acid the relevant parameters are $\angle\text{ONO} = 130° \pm 20'$, and $r_0(\text{N–O}) = 1{\cdot}206 \pm 0{\cdot}005$ Å. Very similar results have been found for nitryl chloride,[7] namely, 130° 35′ ± 15′ and 1·202 ± 0·001 Å. Smith and Magnuson,[8] in their work on nitryl fluoride NO_2F, assumed $\angle\text{ONO} = 125°$ and obtained $r_0(\text{N–O}) = 1{\cdot}23$ Å. It is easily shown from their moments of inertia that, with $\angle\text{ONO} = 130°$, the value $r_0(\text{N–O}) = 1{\cdot}207$ Å. A similar assumption with the data [9] on $\text{CH}_3{\cdot}\text{NO}_2$ gives a value of $r_0(\text{N–O}) = 1{\cdot}204$ Å. These results are summarised in Table 3. The distances $\text{O}_\text{A}\text{–O}_\text{B}$ are not dependent on any structural assumption. The dihedral angle is known reliably only in the case of NO_2Cl, but the close agreement with the other data suggests that these may be good parameters of the nitro-group.

Determination of the Dipole Moment of Nitric Acid.—The dipole moment of HNO_3 was determined from the Stark effect of the transitions $J = 1_{11} \longleftarrow 0_{00}$ and $1_{01} \longleftarrow 0_{00}$. The value obtained was confirmed with the aid of the transition $2_{11} \longleftarrow 2_{12}$. The sample pressure was increased to 20×10^{-3} mm. Hg in order to broaden the hyperfine structure of the transitions. The quadrupole interaction was thereafter ignored, it being more than a power of 10 smaller than the Stark splitting. The ratio E/V, where E (v/cm.) is the average field strength in the wave-guide when the applied voltage is V (v), was determined from the Stark effect of the transition $\text{CH}_3{}^{79}\text{Br}$ $J = 1 \longleftarrow 0 = 18{,}992{\cdot}36$ Mc./sec. This

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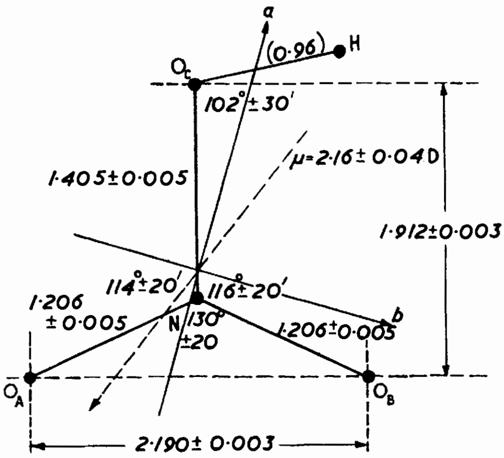
[6] Darling and Dennison, *Phys. Rev.*, 1940, **57**, 128.
[7] Millen and Sinnott, *J.*, 1958, 350.
[8] Smith and Magnuson, *Phys. Rev.*, 1952, **87**, 226.
[9] Tannenbaum, Myers, and Gwinn, *J. Chem. Phys.*, 1956, **25**, 42.

line was chosen instead of the more usual OCS $J = 2 \longleftarrow 1$ transition, as the Stark shift was approximately five times greater than that of the latter at a given field strength. Quadrupole effects in the ^{79}Br nucleus may be ignored since the upper state involved in this transition was shown to be unaffected by the applied field. The dipole moment [10] of CH_3Br is $1{\cdot}797 \pm 0{\cdot}015$ D. The experimental values of the Stark effect in the $J = 1 \longleftarrow 0$ transition of the $H^{14}NO_3$ were: $1_{01} \longleftarrow 0_{00}$, $\Delta\nu/E^2 = (0{\cdot}3033 \pm 0{\cdot}001) \times 10^{-4}$ and, for $1_{11} \longleftarrow 0_{00}$, $\Delta\nu/E^2 = (0{\cdot}1703 \pm 0{\cdot}001) \times 10^{-4}$ Mc./sec. cm.^{2} v^{-2}.

Structure of the nitric acid molecule.



The values for the components of the dipole moment along the *a*- and the *b*-axis were $\mu_a = 1{\cdot}99$, $\mu_b = 0{\cdot}83$ D, whence the resultant dipole moment $\mu = (\mu_a{}^2 + \mu_b{}^2)^{1/2} = 2{\cdot}16 \pm 0{\cdot}02$ D. The resultant dipole moment was calculated to be inclined at an angle $\tan^{-1} \mu_b/\mu_a = 22{\cdot}7° \pm 0{\cdot}5°$ to the *a*-axis. The angle between the resultant dipole moment and the NO_c bond (see Fig.) was therefore $22{\cdot}7° \pm 16°$ since this bond is inclined at an angle of $\sim$16° to the *a*-axis. It was inferred that the angle between μ and NO_c was $39° \pm 2°$, as shown in the Fig., since this would cause μ_a to increase at the expense of μ_b on deuteration. A decrease in μ_b on deuteration was inferred from the fact that the type-*b* spectrum of DNO_3 was considerably weaker than expected.

Experimental.—Part of the work described herein was carried out with the spectrometer constructed by Dr. C. C. Costain at the National Research Council, Ottawa. This spectrometer has been described,[11] as has that built in London.[7]

Nitric acid was prepared from potassium nitrate (1 pt.) and fuming sulphuric acid (2 pts. by wt.); anhydrous nitric acid distilled off at 30—40°/$\sim$0·1 mm. Deuterosulphuric acid and $K^{15}NO_3$ were supplied by Merck and Co. Ltd., Montreal.

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[10] Shulman, Townes, and Dailey, *Phys. Rev.*, 1950, **78**, 145.

[11] Costain and Stoicheff, *J. Chem. Phys.*, 1959, **30**, 308.