819. *Infra-red Spectrum of Nitric and of Deuteronitric Acid Vapour. Completion of Identification of the Fundamental Frequencies. Entropy of Nitric Acid. Barrier Resisting Rotation of the Hydroxyl Group.*

By (the late) HENRY COHN, C. K. INGOLD, and H. G. POOLE.

The infra-red spectra from 3700 to 440 cm.$^{-1}$ of nitric and deuteronitric acid as vapour are recorded and interpreted. Those fundamental frequencies which previous study of the Raman spectra of these acids had left unknown or doubtful have been found and identified, and those assignments of previously observed frequencies which had remained dubious have been settled. The derivation of thermodynamic quantities is illustrated by a calculation of the entropy of nitric acid, which agrees well with the calorimetric value.

The barrier resisting rotation of the hydroxyl or deuteroxyl group about the NO bond in the gaseous molecules is computed, from the torsional frequencies and entropy, to be in the neighbourhood of 10 kcal./mole. This large value is ascribed to internal hydrogen-bonding in the gas molecules. The frequency differences between vapours and liquids can be understood to result from intermolecular hydrogen-bonding in the liquid acids.

THE Raman spectrum of nitric acid has been recorded by many observers. These investigations have recently been reviewed and discussed (Ingold and Millen, *J.*, 1950, 2612). Most of the fundamental frequencies of the nitric acid molecule can be identified in the Raman spectrum, but not all of them. Consequently the spectroscopic information thus secured is insufficient to permit a satisfactory calculation of thermodynamic properties of nitric acid, such as the entropy.

All those fundamental frequencies which are too weak to be observed, or easily observed, in the Raman spectrum of nitric acid, are included among those which are expected to appear strongly in the infra-red spectrum. As only one investigation, moreover one made in somewhat difficult experimental conditions, of the infra-red spectrum has yet been recorded (Freymann and Freymann, *Compt. rend.*, 1946, **222**, 1339), the present re-examination of the spectrum was undertaken with the object of securing a complete account of the fundamental frequencies of nitric acid, and thus of providing a means for the evaluation of its thermodynamic properties.

The known Raman spectra are those of liquid nitric acid and liquid deuteronitric acid. We record below the infra-red spectra of nitric acid and deuteronitric acid, each in the form of vapour, as observed on a prism spectrometer over the spectral range 3700—440 cm.$^{-1}$

For purposes of interpretation, we have to take account of the geometry of the nitric acid molecule. Our most direct knowledge of the geometry of the gaseous molecule is that given by its electron-diffraction pattern (Maxwell and Moseley, *J. Chem. Phys.*, 1940, **8**, 742), and summarised in Fig. 1. The position of the hydrogen atom is not determined. Owing to its relative lightness, its exact position is not particularly critical for our conclusions; and therefore, for the purpose of making calculations, we have assigned it an arbitrary position, as indicated in Fig. 1, taking the OH bond-length to be that in water, 0·96 Å, and giving the NOH angle its "theoretical" value, 90°. The angle within the NO_2 group is only approximately determined by the diffraction pattern. Its value is somewhat critical for certain of our conclusions, and we shall later give reason for thinking that, the other dimensions being accepted, 135° would be a better estimate of this angle than 130°.

A recent *X*-ray investigation of the crystal structure of nitric acid has yielded approximate dimensions of the crystal molecule (Luzzati, *Acta Cryst.*, 1951, **4**, 120). The *X*-ray length of the N–(OH) bond is markedly smaller (1·30 ± 0·05 Å) than the electron-diffraction length, while the other geometrical parameters are the same to within the rather wide limits of uncertainty. The difference in the measured N–(OH) lengths may well reflect a real change of molecular form between the gas and the crystal, where, owing to intermolecular hydrogen-bonding, the NO_3 group would probably assume a shape somewhat more like that of the nitrate ion, which has three equal NO bonds. Accordingly, we have preferred to use the electron-diffraction values, in our discussion of the infra-red spectra of gaseous nitric and deuteronitric acid.

Nitric acid, as a penta-atomic molecule, has nine normal modes of vibration. But the hydrogen atom is so much lighter than the other atoms that these vibrations divide themselves fairly sharply into two sets.

In the first set, the OH group will move essentially as a single-atomic unit, the oxygen atom carrying its hydrogen atom with it. As to these vibrations, essentially vibrations of the NO_3 group, the molecule can be represented approximately by a tetra-atomic model, O_2NO', where O′, an imaginary atom of mass 17, does duty for the hydroxyl group. There are accordingly six of these vibrations: they are approximately described by the first six drawings in Fig. 2. They can be regarded as derived from the known vibrations of the nitrate ion, which, as a trigonal tetra-atomic molecule, has four fundamental frequencies, but with two degenerate, splitting each into two, so that the total of four becomes six, as soon as one oxygen atom becomes differentiated from the others. The six vibrations can be approximately described, three as stretching, and two as bending vibrations, and one as an out-of-plane deformation. By assuming the symmetry C_{2v}, with the NO′ bond, representing the N–(OH) bond, as the two-fold axis (hereafter called the C_{2v} axis), the vibrations can be given an alternative approximate description: two stretching and one bending vibration are totally symmetrical (A_1) with respect to the assumed symmetry, one stretching and one bending vibration are non-totally symmetrical but planar (B_2), while the one out-of-plane vibration stands alone in its symmetry class (B_1). The corresponding six vibrations of deuteronitric acid could be similarly represented by the model O_2NO', where O′ now has mass 18. Obviously the isotopic change will not greatly affect the frequencies of any of these vibrations.

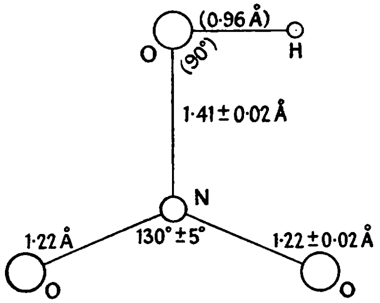


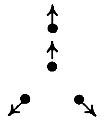
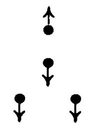
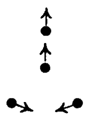
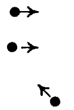
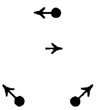
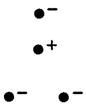
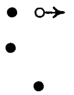
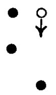
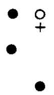
FIG. 1. *Model of the nitric acid molecule.*

(The geometrical parameters are as determined by Maxwell and Moseley, except those in parentheses, which are assumed.)

In the second set of vibrations of nitric acid, nearly all the motion will be in the hydrogen atom, the NO_3 group remaining nearly rigid. There will be three of these vibrations, corresponding to the three degrees of freedom of motion of the hydrogen atom, as indicated in the last three drawings of Fig. 2. These vibrations can be approximately described as the stretching, bending, and twisting vibrations of the hydrogen atom. Under the symmetry C_s of the model of Fig. 1, the stretching and bending vibrations of hydrogen belong to the planar class (A'), while the twisting vibration belongs to the out-of-plane class (A'') of vibrations. The corresponding vibrations of deuteronitric acid will be similar, most of the motion being in the deuterium atom. Hence the isotopic change will strongly alter the frequencies of these vibrations.

The drawings of Fig. 2 are labelled in accordance with Redlich and Nielsen's scheme of numbering of the vibrations of nitric acid (*J. Amer. Chem. Soc.*, 1943, 65, 654). In closer approximation than Fig. 2 describes, the two planar hydrogen C_s vibrations, nos. 7 and 8, belonging to class A', can mix, in principle at least, with the five planar C_{2v} vibrations nos. 1—5, of classes A_1 and B_2, which classes are to this extent not quite sharply separated from each other; while the out-of-plane hydrogen C_s vibration, no. 9, belonging to class A'', can mix with the out-of-plane C_{2v} vibration, no. 6, of class B_1. But in practice the relative lightness of the hydrogen atom will militate against such mixings, as also will the outstandingly high value of the frequency of the hydrogen stretching vibration, no. 7, and the outstandingly low value of the frequency of the hydrogen twisting vibration, no. 9. It is the hydrogen-bending vibration, no. 8, of medium frequency, which is susceptible of most mixing particularly, as we must expect, with the less symmetrical of the other planar-bending frequencies, no. 5.

FIG. 2. *Normal vibrations and observed frequencies (cm.$^{-1}$) of nitric acid.*

O_2NO' model[1]			
No. and C_{2v} class	1. (A_1)	2. (A_1)	3. (A_1)
Description	NO_2-stretching	NO'-stretching	NO_2-bending
HNO_3 Raman (liq.)[3]	1300 (*s, p*)	925 (*s. p*)	680 (*m, p*)
Infra-red (vap.)[5]	1320 (*s, o*)	886 (*s, q*)	—
DNO_3 Raman (liq.)[4]	1300 (*s*)	915 (*s*)	670 (*m*)
Infra-red (vap.)[5]	1313 (*s, q*)	888 (*s, q*)	—
O_2NO' model[1]			
No. and C_{2v} class	4. (B_2)	5. (B_2)	6. (B_1)
Description	NO_2-stretching	ONO'-bending	Out of plane
HNO_3 Raman (liq.)[3]	1675 (*m, d*)	610 (*m, d*)	(767)[6]
Infra-red (vap.)[5]	1710 (*s*)	583 (*m, q*)	765 (*m*, ***Q***)
DNO_3 Raman (liq.)[4]	1645 (*m*)	580 (*m*)	(767)[6]
Infra-red (vap.)[5]	1685 (*s*)	543 (*m, q*)	764 (*m*, ***Q***)
H–R model[2]			
No. and C_s class	7. (A')	8. (A')	9. (A'')
Description	H-stretching	H-bending	H-twisting
HNO_3 Raman (liq.)[3]	3400 (band)	—	480 (*w*)[7]
Infra-red (vap.)[5]	3560 (*m*)	1335 (*s, q*)	465 (*s*, ***Q***)
DNO_3 Raman (liq.)[4]	2470 (band)	—	370 (*w*)[7]
Infra-red (vap.)[5]	2627 (*m, Q*)	1014 (*s, q*)	(*ca.* 365)[8]

Notes. [1] In these drawings the uppermost mass-point represents the hydroxyl group moving as a single unit. [2] In these drawings the hollow circle represents the hydrogen atom moving relatively to a rigid NO_3 group. [3] As adopted by Ingold and Millen (*loc. cit.*). [4] Bannerji and Mishra, *Indian J. Phys.*, 1941, **24**, 359; Redlich and Nielsen, *J. Amer. Chem. Soc.*, 1943, **65**, 654. [5] This investigation. [6] Not directly observed; deduced from first overtone observed at 1535 cm.$^{-1}$ in the Raman spectrum of both HNO_3 and DNO_3. [7] Recorded by Redlich and Nielsen only (*loc. cit.*). [8] Not observed: estimated from a combination band.

s = strong
p = polarised
Q = medium *Q* branch
m = medium intensity
d = depolarised
q = weak *Q* branch
w = weak
Q = strong *Q* branch
o = no *Q* branch

Under the drawings in Fig. 2 are entered the known Raman fundamental frequencies, as measured in liquid nitric acid and liquid deuteronitric acid. The frequencies assigned to vibrations nos, 1—7 are as given by Ingold and Millen (*loc. cit.*), in agreement with most previous authors. Special comment is necessary on the Raman frequencies of three vibrations.

The frequency of the out-of-plane vibration, no. 6, of nitric acid was for some time doubtful, as Ingold and Millen have recounted; but they should have pointed out in that connexion that, after Freymann and Freymann had observed (*loc. cit.*) an infra-red band in nitric acid vapour at about 780 cm.$^{-1}$, and had suggested that this might be the fundamental band of vibration no. 6, Redlich (*J. Amer. Chem. Soc.*, 1947, **69**, 2240), correcting Redlich and Nielsen's earlier assignment of the Raman frequency 1535 cm.$^{-1}$ to this vibration (*loc. cit.*), recognised the latter frequency at its first overtone, a conclusion supported also by Ingold and Millen. The same conclusion applies to the same Raman frequency of deuteronitric acid.

The frequency of the hydrogen-bending vibration, no. 8, has remained controversial up to the present. Redlich and Nielsen assumed that the line at 1675 cm.$^{-1}$ in the Raman spectrum of nitric acid was double, and that its second component belonged to this vibration. However, their spectrogram showed no signs of the assumed doubling. For the same vibration of deuteronitric acid, they offered a frequency of about 1340 cm.$^{-1}$, represented by a bulge on the microphotometric contour of the strong Raman line at 1300 cm.$^{-1}$. Ingold and Millen could find no signs of a doubling of the Raman frequency 1675 cm.$^{-1}$ of nitric acid. And as to the bulge given by deuteronitric acid, Ingold and Millen found a similar bulge at about 1360 cm.$^{-1}$ on the contour of the strong line at 1300 cm.$^{-1}$, in the Raman spectrum of ordinary nitric acid. It seemed obvious that the two bulges had a common origin, as first overtones of vibration no. 3. The conclusion was, therefore, that the fundamental frequencies of vibration no. 8 had not been observed in Raman spectra. It was noted that they should be weak in Raman, but strong in infra-red spectra; and it was stated that they would be sought by an investigation of the latter. These frequencies have now been located in the infra-red; and, as Ingold and Millen suspected, they are different from the frequencies which had previously been under consideration.

Redlich and Nielsen observed a weak and diffuse line at about 480 cm.$^{-1}$ in the Raman spectrum of liquid nitric acid and one at about 370 cm.$^{-1}$ in that of liquid deuteronitric acid. They assigned these frequencies to the hydrogen-twisting vibration, no. 9. On Ingold and Millen's plates the records of this vibration were too vestigial to justify any firm conclusion. It was noted only that the frequencies should be weak in the Raman spectrum but strong in the infra-red, and it was stated that they would be sought in the latter spectrum. The present study of the infra-red spectrum of nitric acid vapour makes it certain that Redlich and Nielsen's observation and interpretation of these frequencies in the Raman spectra were correct.

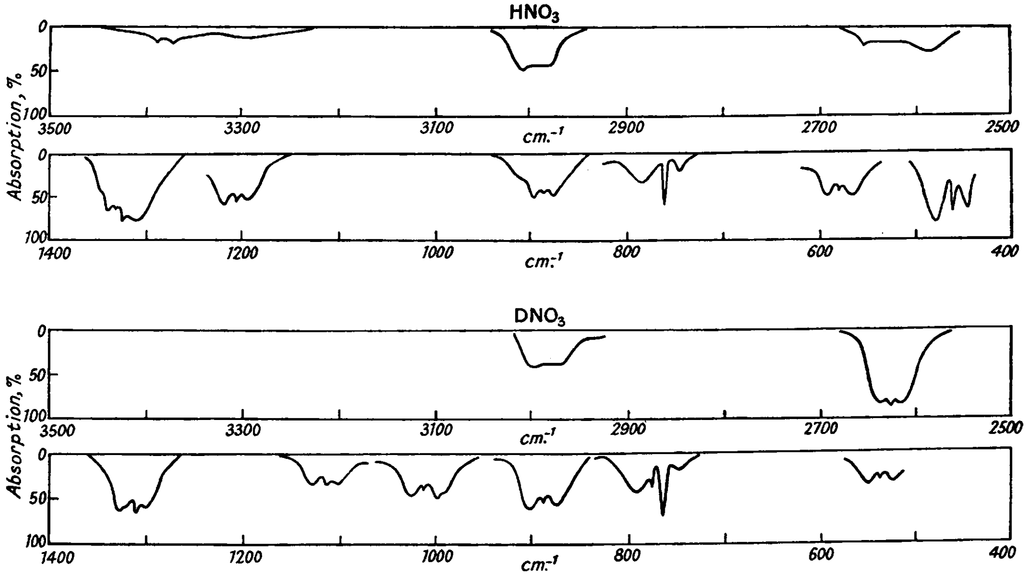
The geometry of the nitric acid molecule is relevant to the study of the rotational contours of the vibrational bands in the infra-red spectrum, because any such contour is determined by the magnitudes of the three principal moments of inertia, and by their directions, relatively to that along which the electric moment oscillates in consequence of the vibration.

Nitric acid is an asymmetric top; but its mass distribution is not very different from that of the nitrate ion, which is a symmetric top, with two principal moments of inertia each equal to half the third. In nitric acid, the two smaller principal moments of inertia are nearly equal, and the third principal moment of inertia is equal to their sum.

The band envelopes for different types of asymmetric top have been described (Badger and Zumwalt, *J. Chem. Phys.*, 1936, **6**, 711). For molecules of the type of nitric acid, which approximates to a plane symmetric top, the envelopes can take the following forms. (1) For a vibration in which the oscillating electric moment makes a small angle with the axis of the smallest of the principal moments of inertia, the bands will have a Q branch of the same order of intensity as the P and R branches. (2) For a vibration whose electric moment makes a small angle with the axis of the intermediate moment of inertia, the bands will have P and R branches with a central minimum, or at most a small Q branch. (3) For a vibration whose electric moment makes a small angle with the axis of the greatest principal moment of inertia, the bands will have P and R branches separated by an outstandingly strong and sharp Q branch.

In nitric acid the axis of the greatest moment of inertia is certainly at right angles to the molecular plane. However, as to the two axes in the molecular plane, there could be dubiety as to whether that of the smallest moment of inertia approaches more closely to the C_{2v} axis, or to a direction at right-angles to the latter. In this matter the angle within the NO_2 group could be critical. If the angle is 130°, then, for both nitric acid and deuteronitric acid, according to the model in Fig. 1, the axis of the smallest moment of inertia makes an angle of about 35° with the C_{2v} axis, while the other moment of inertia with an axis in the molecular plane is about 10% larger. If the angle is 135°, then for both acids, the axis of the intermediate moment of inertia makes an angle of roughly 35° in the opposite sense, with the C_{2v} axis, and the other moment of inertia with an axis in the molecular plane is about 10% smaller. The calculated magnitudes and directions of the principal moments of inertia of nitric acid, and of deuteronitric acid, for the two assumed NO_2 angles, are given in Table 1.

FIG. 3. *Infra-red absorption bands of nitric and deuteronitric acid vapours*



(The conditions of measurement of each band are as given in Tables 2 and 3. It is to be noted that the conditions are not the same for all the bands, so that relative intensities must be judged with reference to the Tables.)

TABLE 1. *Principal moments of inertia* (I_2 *in g.-cm.*^{2}) *of the molecules of nitric and deuteronitric acids, two different* NO_2 *valency angles* (θ) *being assumed.* (I_y *lies in the molecular plane at right-angles to* I_x. I_z *is directed perpendicularly to the molecular plane.*)

θ	Isotope	Angle ($\widehat{I_xC_{2v}}$)	$10^{40}I_x$	$10^{40}I_y$	$10^{40}I_z$
130°	HNO_3	35°	65·0	71·3	136·3
	DNO_3	38°	64·7	74·4	139·1
135°	HNO_3	−30°	70·4	64·8	135·2
	DNO_3	−40°	73·5	64·1	137·6

Now although the forms of band envelopes furnish one of the criteria which help us to assign infra-red bands to their vibrations, we have other means of doing this in the case of nitric and deuteronitric acids, *e.g.*, by comparisons with the Raman spectra of these acids, already fairly completely understood, and by comparisons with the understood Raman and infra-red spectra of the nitrate ion. Thus the infra-red spectra of nitric and deuteronitric acids themselves allow us to form an opinion as to whether the axis of the smallest, or that of the intermediate moment of inertia forms the smaller angle with the C_{2v} axis. The spectra show that it is the axis of the intermediate moment of inertia which does so, and that therefore, the other geometrical parameters of Fig. 1 being accepted, the angle 135° is the better value of the valency angle within the NO_2 group.

Freymann and Freymann (*loc. cit.*) examined the infra-red spectrum from 1600 to 600 cm.$^{-1}$ of nitric acid vapour enclosed between rock-salt plates. These were rapidly attacked by the acid with the production of a nitrate ion spectrum. However, the following observed bands were attributed to nitric acid :

683, 780, 905, (?) 1258, (?) 1572 cm.$^{-1}$

We confirm the second and third of these bands, but not the first, even though there is a Raman frequency of nitric acid having just this value, while the fourth and fifth were not observed by us, unless they correspond to bands which we found at considerably higher frequencies.

Our infra-red frequencies of nitric and of deuteronitric acid, as measured in vapour enclosed between silver chloride plates, and also the particulars of the conditions in which the bands were measured are recorded in Tables 2 and 3, while the forms of the bands, as far as we determined them, are shown in Fig. 3. The last column of either Table contains our assignment of the frequencies to fundamental vibrations or to combination tones. The assignments are given in terms of the numerical labels in Fig. 2.

TABLE 2. *Infra-red absorption bands of nitric acid vapour.*

Frequency (cm.$^{-1}$)	Cell-length (cm.)	Temp. of liquid acid	Slit-width (mm.)	Prism	Assignment
3560	8	20°	0·03	SiO_2	(7)
3390	15	,,	0·06	CaF_2	2 × (4)
3000	,,	,,	0·07	,,	(1) + (4)
⎧2627	,,	,,	0·08	,,	2 × (1)
⎩2585	,,	,,	,,	,,	(2) + (4)
1710	4	0	0·20	,,	(4)
⎧1335	,,	,,	0·32	,,	(8)
⎩1320	,,	,,	,,	,,	(1)
1206	15	20	0·46	,,	(6) + (9)
886	4	0	0·32	NaCl	(2)
765	13	20	0·34	,,	(6)
583	15	,,	—	KBr	(5)
465	4	0	—	,,	(9)

Note. The braces in the first column denote overlapped bands.

TABLE. 3. *Infra-red absorption bands of deuteronitric acid vapour.*

Frequency (cm.$^{-1}$)	Cell-length (cm.)	Temp. of liquid acid	Slit-width (mm.)	Prism	Assignment
2980	15	20°	0·06	CaF_2	(1) + (4)
2627	8	,,	,,	,,	(7)
1685	4	0	0·16	,,	(4)
1313	,,	,,	0·28	,,	(1)
1114	15	20	0·20	NaCl	(6) + (9)
1014	3	,,	0·24	,,	(8)
888	4	0	0·36	,,	(2)
764	13	20	0·34	,,	(6)
543	15	,,	0·60	KBr	(5)

The assignment of the bands presents no major difficulty. The moderately strong band of nitric acid at 3560 cm.$^{-1}$, as well as that of deuteronitric acid at 2627 cm.$^{-1}$, can at once be assigned to the hydrogen-stretching vibration, no. 7. The contour of the nitric acid band was not determined, but that of the deuteronitric acid band was : it shows P, Q, and R branches of comparable strength, indicating that the oscillating electric moment makes a small angle with the axis of the smallest of the principal moments of inertia. This is in agreement with the already stated conclusion that it is the axis of the intermediate moment of inertia which approximates most closely to the C_{2v} axis, and that, therefore, the wider of the two suggested angles for the NO_2 group of nitric acid is the more nearly acorrect.

The frequencies of the three NO-stretching vibrations, can immediately be recognised, apart from one small detail, by comparison with the Raman spectra, where these frequencies are identified by intensity and polarisation. The strong infra-red band of nitric acid at 1710 cm.$^{-1}$, and that of deuteronitric acid at 1685 cm.$^{-1}$, obviously belong to vibration no. 4. Their band envelopes were not traced in detail. The strong band of nitric acid at 886 cm.$^{-1}$, as well as that of deuteronitric acid at 888 cm.$^{-1}$, equally clearly belong to vibration no. 2. The envelopes of these bands were traced : they have weak Q branches, indicating that the oscillating electric vector is making only a small angle with the axis of the intermediate moment of inertia. In this vibration the oscillating electric moment lies nearly parallel to the C_{2v} axis, and thus we have confirmation of the conclusion that it is the axis of the intermediate moment of inertia which approximates the most closely to this axis. One component of the strong double band of nitric acid at 1320—1335 cm.$^{-1}$, as well as the strong single band of deuteronitric acid at 1313 cm.$^{-1}$, must belong to vibration no. 1. The higher-frequency component of the nitric acid band has a vestigial Q branch, while the lower-frequency component is of irregular form, but seems to have a central minimum. In the band of deuteronitric acid the lateral branches are irregular, but there seems to be a central minimum. Any of these bands would, so far as the band envelopes can indicate, qualify for assignment to a vibration, such as no 1, in which the electric vector oscillates in a direction near to that of the C_{2v} axis, and therefore by our former conclusion, to that of the axis of the intermediate moment of inertia. We cannot unequivocally decide, nor is it important to do so, which of the two overlapped nitric acid bands should be chosen for assignment to vibration no. 1. Provisionally we have chosen the lower frequency, 1320 cm.$^{-1}$, which gives slightly better values for the calculated frequencies of some combination tones, and slightly more probable isotopic relations.

The second of the overlapped bands of nitric acid, that at 1335 cm.$^{-1}$ according to the above selection, must correspond to the single deuteronitric acid band at 1014 cm.$^{-1}$ The latter is the only band in the relevant frequency region, not needed for other correlations and assignments, and, indeed, the only one with the right type of contour. Like the nitric acid band at 1335 cm.$^{-1}$, the deuteronitric acid band at 1014 cm.$^{-1}$ has a very weak Q branch. Therefore our previous conclusions indicate that these frequencies belong to a vibration in which the electric moment oscillates in a direction approximating to that of the C_{2v} axis. The large isotope shift points to a hydrogen vibration. It follows that these frequencies belong to vibration no. 8. The general order of magnitude of the frequencies, the fact that they are weak to invisibility in the Raman spectrum, and the obviousness with which all other infra-red frequencies except these can be otherwise assigned, all support the conclusion stated.

The frequencies of the bending vibrations, nos. 3 and 5, of the NO_3 group are found in the Raman spectra, where they are clearly distinguished by polarisation. In the relevant region of either infra-red spectrum, only one band appears, in that of nitric acid at 583 cm.$^{-1}$, and in that of deuteronitric acid at 543 cm.$^{-1}$. These bands must belong to vibration no. 5. It is not inconsistent that, in our records of these bands, the Q branches appear to be weaker than the P and R branches, instead of being of the same order of intensity, as is expected for a vibration, such as no. 5, in which the oscillating electric moment is nearly perpendicular to the C_{2v} axis, and therefore nearly parallel to the axis of the smallest moment of inertia. For here, in the potassium bromide range of the spectrum, the low energy in the incident radiation necessitates the use of a slit so wide open that it cannot scan the Q-branch without including parts of the lateral gaps, and therefore records the Q branch with too small an intensity. Vibration no. 3 seems to be too weak in the infra-red to be observed with our equipment : presumably the change of electric moment is quite small in this vibration. It should be mentioned that Freymann and Freymann record an infra-red band of nitric acid in just the right position, namely, at 683 cm.$^{-1}$; but with three times their path-length, we could not find it. We could find a band at 650 cm.$^{-1}$, but the variability of its intensity showed that it did not belong to nitric acid, and we assign it as the strong bending frequency of nitrogen dioxide, a small amount of which often appears in the vapour of nitric acid. Freymann and Freymann were working in the presence additionally of the nitrate-ion band at 720 cm.$^{-1}$, and hence the actual appearance of their spectrum, in the region of the claimed nitric acid band, must have been rather complicated.

The frequencies of the out-of-plane vibration, no 6, of the NO_3 group are clearly identified by the outstandingly strong and sharp Q branches of the nitric acid band at 765 cm.$^{-1}$

and the deuteronitric acid band at 764 cm.$^{-1}$: the vibrating electric moment is now nearly parallel to the axis of the greatest moment of inertia. These frequencies occur too weakly for observation in Raman spectra, but can be deduced from observed Raman overtones.

The frequency of the hydrogen twisting vibration, no. 9, in which also the oscillating electric moment is nearly parallel to the axis of the greatest moment of inertia, is clearly identified for nitric acid by the sharp, prominent, Q branch of the band at 465 cm.$^{-1}$. It must be remembered that the real peak intensity of the Q branch of this band of the potassium bromide region must be much greater than the intensity with which, owing to the large slit-width used, the Q branch appears in our record. The corresponding band of deuteronitric acid lay outside the spectral range of our equipment, consistently with its assignment to a hydrogen vibration, having a large isotopic shift. From an infra-red combination tone, the frequency can be roughly (say to ± 10 cm.$^{-1}$) estimated as 365 cm.$^{-1}$. The frequencies of this vibration have already been identified by Redlich and Nielsen in Raman spectra, but owing to the extreme weakness with which they there appear, the present confirmation is useful.

Several combination bands have been measured. Our assignments of them are in Tables 2 and 3.

The frequency differences between vapour and liquid (see Fig. 2) deserve remark: all can be qualitatively understood as arising from intermolecular hydrogen bonding in the liquid. The stretching frequencies of the NO_2 group (vibrations nos. 1 and 4) are reduced on passing from the vapour to the liquid, obviously because, outside each oxygen atom, the hydrogen atom of another molecule is furnishing a restoring force opposite to that of the covalent bond. The stretching frequency of the N–(OH) bond (vibration no. 2) is, however, raised in the liquid, presumably because the oxygen atom is to some extent anchored by the rather closely fixed position, which its laterally bonded hydrogen atom assumes on account of hydrogen-bonding; and perhaps because the oxygen atom itself is anchored by hydrogen-bonding on the side opposite to the covalently bound hydrogen atom. The bending frequency of the O–N–(OH) angle (no. 5) is raised in the liquid—a result which we would expect also for the bending frequency of the O–N–O angle (no. 3), if the observations could be made—because all the oxygen atoms will be directly or indirectly anchored against lateral motion by hydrogen-bonding. The out-of-plane vibration of the NO_3 group shows no change of frequency from vapour to liquid, presumably because nearly all the motion is in the nitrogen atom, which, moving through the plane of the other atoms, is free from hydrogen-bonding. The hydrogen-stretching vibration (no. 7) has its frequency reduced and spread in the liquid, because hydrogen bending opposes various restoring forces to that of the covalent bond. The hydrogen-twisting frequency (no. 9) is increased and spread in the liquid—and we should expect the same result for the hydrogen-bending frequency (no. 8), if we could make the necessary observations—because of the anchoring effect of hydrogen-bonding on lateral hydrogen motion.

As to the isotopic frequency-shifts (see Fig. 2), the Teller–Redlich rule for the isotopic ratios of frequency products is not very useful in application to nitric acid, because, owing to the low symmetry of that molecule, it handles the frequencies in considerable sets. However, Redlich and Nielsen have shown (*loc. cit.*) that the planar Raman frequencies of nitric acid and deuteronitric acid are consistent with the rule. The same is true for the infra-red frequencies.

More interesting information is afforded by some of the individual isotopic frequency shifts. Such shifts measure the amount of motion suffered by the hydrogen atom in the vibration; but, if the hydrogen motion is sufficient to produce a considerable shift, then, on account of amharmonicity in the potential function, the actual shift may be somewhat different from, and is usually a little less than, that computed for harmonic motion.

If the six vibrations (nos. 1—6) of the NO_3 group were completely uncoupled from the three hydrogen vibrations (nos. 7—9), so that in the former set of vibrations the OH group moved exactly as an atom, then the isotope shifts in these vibrations would be small. By neglecting changes of coupling within the set of NO_3 vibrations, it can be computed that none of the shifts would be above 2·0%, the maximum applying to the hypothetical case in which both the OH and NO_2 groups move like single atoms. In fact, five of the six vibrations of the NO_3 group show frequency shifts in the range 0·0 to 1·5%. But one vibration, no. 5, shows a shift of 7%, or more accurately, an isotopic ratio, H : D, of 1·074. Here there must be considerable coupling with one of the hydrogen vibrations. Now if the hydrogen-bending vibration, no. 8, were fully uncoupled from all other vibrations, and also were strictly harmonic, then its isotopic ratio would be 1·403. The observed ratio is only 1·316. That is, the isotopic shift is 7% too small for a pure hydrogen vibration. Thus, a transfer of shift between vibrations nos. 5 and 8 seems to have occurred, and we may reasonably attribute this to the appreciable coupling between these vibrations, which was expected (p. 4274) on the basis of a general consideration of the mechanics of the nitric acid molecule.

If the hydrogen-stretching vibration, no. 7, were fully uncoupled and harmonic, its isotopic ratio, H : D would be 1·388. The observed ratio is 1·355. The defect of 2% is not markedly greater than the defect expected to arise from Morse-curve anharmonicity. It is possible, however, that some of the observed small defect comes from very weak coupling between this vibration and others.

If the hydrogen-twisting vibration, no. 9, were fully uncoupled and harmonic, its isotopic ratio would be 1·397. The observed ratio is only about 1·27, a defect of about 9%. It is unlikely that more than a small part of this defect is due to coupling with other vibrations. Certainly there is no transfer of isotopic shift to the only other vibration of the same symmetry class, namely, vibration no. 6, which in fact shows no shift. Therefore we attribute the large defect in the frequency shift of vibration no. 9 to an abnormal anharmonicity. This is inconsistent with our picture of the twisting vibration as a restricted rotation, for which the potential-energy hollow has a more open shape than either a parabola or a Morse curve, and is, indeed, usually thought to resemble a cosine curve. In such more open hollows, the energy level of the greater-amplitude quantum of the lighter isotopic form can drop down rather closer to that of the smaller-amplitude quantum of the heavier form, thus giving an abnormally small frequency ratio.

By assuming a rotation-restricting barrier of cosine form with two minima, and then neglecting anharmonicity up to the level of the first quantum of torsional oscillation, one may use the frequency of the latter, in order to make a rough computation of the barrier height. The formula is

$$\omega + 6{\cdot}223\ (V/10^{40}I)^{\frac{1}{2}}$$

where ω is the frequency in wave-numbers, V is the barrier height in cal./mole, and I is the " reduced " moment of inertia, that is, $I_1I_2/(I_1 + I_2)$, where I_1 and I_2 are the moments of the groups of OH and NO_2 for independent rotations about the bond between them. With dimensions as in Fig. 1, except that the angle of the NO_2 group is taken as 135°, I has the value of $1{\cdot}50 \times 10^{-40}$ g.-cm.^{2} The observed torsional frequency for nitric acid, 465 cm.$^{-1}$, then leads to the estimated barrier height, 8·4 kcal./mole. Because of the neglect of anharmonicity in the troughs of the potential-energy curve, this estimate is likely to be too low. Hence it is already obvious that the barrier is much larger than those found in simple organic molecules, such as ethane, methylamine, and methyl alcohol, or even in somewhat more complicated ones, such as *neo*pentane, trimethylamine, and methyl ether, none of which has a barrier higher than 4 kcal./mole.

We can carry the study of the barrier a little further by calculating the entropy of nitric acid from the molecular dimensions and our now complete set of frequencies (convenient formulæ and tables are given by Bright Wilson, *Chem. Reviews*, 1940, **27**, 17), and by comparing the result with the calorimetric value of the entropy (Forsyth and Giauque, *J. Amer. Chem. Soc.*, 1942, **64**, 48). This comparison is in Table 4.

The agreement is as good as the estimated accuracy of the calorimetric value. If we treat the latter as accurate, and also regard all the entropy contributions derived from molecular data as accurate, except that coming from the torsional vibration (no. 9), then we can obtain the entropy contribution of the latter by difference, and from this compute the cosine barrier-height, without using the torsional frequency, and therefore without committing the probably appreciable error of neglecting its anharmonicity. By difference we have for the entropy contribution, 0·67 cal./mole-deg., and from this, with the aid of

TABLE 4. *Standard entropy at* 298·1° K *of nitric acid vapour* (S^0 *in cal./mole-deg.*) *as calculated from molecular quantities with neglect of gas-imperfection and anharmonicity, and as obtained calorimetrically.*

Vibrational entropy

No.	1	2	3	4	5	6	7	8	9
cm.$^{-1}$	1320	886	680	1710	583	765	3560	1335	465
S^0	0·03	0·15	0·33	0·00	·047	0·24	0·00	0·03	0·75

Total entropy

Translational	38·25	cal./mole-deg.
Rotational	23·35	„
Vibrations nos. 1—8	1·25	„
Vibration no. 9	0·75	„
Total calculated entropy	63·70	„
Calorimetric value (Forsyth and Giauque)	63·62 ± 0·10	cal./mole-deg.

Pitzer's thermodynamic tables for cosine barrier oscillators (*J. Chem. Phys.*, 1937, **5**, 469), we find the barrier height 10·2 kcal./mole.

However we compute it,* the energy barrier is clearly too large to be credited to the type of force, probably a repulsive force, which sets up barriers of 1—4 kcal./mole against torsional hydrogen motion in simple saturated organic molecules. Forsyth and Giauque (*loc. cit.*), though they had incomplete spectral data, realised that a considerable torsional barrier existed in the nitric acid molecule, and suggested internal hydrogen-bonding as a possible cause. There must, of course, be electrostatic attraction between the hydrogen atom and both non-hydroxyl oxygen atoms in all orientations of the hydroxyl group: such binding, if strong enough, could overcome the usual sort of repulsive force in the two planar orientations, producing energy minima in these configurations, and energy maxima in the intervening perpendicular orientations. In order to see whether such forces could conceivably produce a barrier of the right size, let us make an approximate calculation of the difference of electrostatic energy between the planar and perpendicular orientations. For this purpose, we take the electric moment of the hydroxyl bond as 1·5D, a value which suits the dipole moments of water and alcohols, and assume for simplicity that electric charges giving this moment are located at the hydrogen and oxygen nuclei, while a charge of half an electron, arising from the split dipolar bond, is situated at each of the other oxygen nuclei. The bond lengths and bond angles being taken as heretofore, the electrostatic barrier height then works out to 14·5 kcal./mole. Of course, this type of calculation is very rough; but it does suffice to show that electrostatic binding could, possibly after overcoming the more usual barrier-giving forces of opposite sign, produce a torsional barrier, such as that to which the observations point, with a height of the order of 10 kcal./mole.

EXPERIMENTAL

Pure nitric acid and dinitrogen pentoxide were made as described in earlier papers from these laboratories, while deuteronitric acid was prepared by carefully regulated interaction of the pentoxide with deuterium oxide of 99·6% isotopic purity.

The spectra were recorded on a Hilger D 209 spectrometer, with the prisms and slit-widths specified in Tables 2 and 3.

The cells had silver chloride windows, each about 20 mm. × 25 mm. and 1 mm. thick. Otherwise they consisted only of glass and " polythene." Each window was sealed, by means of a cement of molten " polythene, " on to the edges of a hole cut out of the centre of a " polythene " disc of about 5 mm. thickness. The disc was similarly sealed to the rim of the glass cylindrical wall of the cell. This wall carried a branched side-tube : one branch led through a B24 ground joint to a bulb containing the liquid acid, while the other branch led through a tap

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* If we had used the dimensions of the crystal molecule of nitric acid (Lazzati, *loc. cit.*) for calculating the rotational entropy of the gaseous molecule when computing the entropy of torsional motion from calorimetric data, the torsional entropy would have been 0·80 cal./mole-deg., and the barrier height 9·2 kcal./mole. Having passed from the frequency direct to the entropy as in Table 4, with neglect of anharmonicity, if we had proceeded from this value to the barrier height with the aid of Pitzer's tables, the value would have been 9·6 kcal./mole.

to the vacuum pump. The acid was held at liquid-air temperature during evacuation of the cell, in preparation for a set of spectral observations.

After making a general survey of a spectrum, the individual bands were examined, by choosing for each a cell of suitable length, and by operating at a suitable vapour pressure, the latter regulated by controlling the temperature of the liquid acid. The object of setting up these conditions, which are specified in Tables 2 and 3, was to produce records showing between 30% and 80% maximum absorption. The practice was to run through the part of the spectrum under investigation, with the conditions thus chosen, and then, without altering the position of the cell, to put a bath of liquid air round the side-bulb, and run through the spectral range again, in order to record the background.

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