510. *Vibrational Spectra of Ionic Forms of Oxides and Oxy-acids of Nitrogen. Part V. Raman Spectral Evidence of the Ionisation of Dinitrogen Pentoxide in Nitric Acid, and of the Constitution of Anhydrous Nitric Acid.*

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With the aid of previous, and of some new, observations, the Raman spectra of nitric acid and of the nitrate ion are considered, separately and in combination; and the conclusions are used in order to interpret spectral evidence concerning the condition of dinitrogen pentoxide in nitric acid, and the self-dissociation of nitric acid.

The vibrational assignment of observed bands in the Raman and infra-red spectra of nitric acid has been completed. The key to the problem is the Raman line at 1535 cm.$^{-1}$. It is assigned as the first overtone, by which the out-of-plane vibration of the NO_3 group is expected to be more strongly represented in the Raman spectrum than by its fundamental frequency. This agrees with the polarisation, and the lack of a hydrogen-isotope shift, of the line, and with the existence in the infra-red, but not in the Raman, spectrum, of the corresponding fundamental frequency. This decided, all other details of these spectra fall easily into place. The three chief Raman frequencies of the nitrate ion have an agreed assignment to the three planar fundamentals of the ion; and the fourth observed Raman frequency, 1665 cm.$^{-1}$, is again assigned as the first overtone of the out-of-plane vibration, the fundamental frequency of which should occur, and is known, in the infra-red. The nitrate ion, when present to the extent of some units % in nitric acid, can be recognised indubitably by its Raman spectrum.

In the Raman spectrum of dinitrogen pentoxide in solution in nitric acid, the nitronium ion and the nitrate ion are completely identified; and their spectra are shown to account for the whole of the solute. No trace of the known spectrum of the covalent dinitrogen pentoxide molecule is found. It is concluded that dinitrogen pentoxide is a strong electrolyte in nitric acid, the ions of the dissolving solid falling apart without covalency change, as when sodium chloride dissolves in water. Analytically anhydrous nitric acid is shown by its Raman spectrum to contain about 2·5% of dinitrogen pentoxide and 0·5% of water—estimates which are in satisfactory agreement with those determined cryoscopically (*J.*, 1950, 2552).

(1) *Raman Spectrum of Nitric Acid.*

(1.1) *General Survey of Frequency Assignments.*—For the purposes of the analyses given later in this paper, it will be necessary to have arrived at a complete understanding of those Raman frequencies of nitric acid which belong to the molecular form of the acid.

The Raman spectrum of nitric acid has been described by a number of investigators. There is general agreement as to the main frequencies which are given below in cm.$^{-1}$, along with the usual qualitative indications of intensity (cf. Part I). The frequencies belonging to molecular nitric acid, whose assignment to vibrations is first to be discussed, are in the first row. The two frequencies in the second row do not belong to molecular nitric acid :

610 (ms)	680 (ms)	925 (s)	1300 (vs)	1535 (w)	1675 (m)	3400 (band)
		1050 (w)		1400 (w, sharp)		

(Rao, *Nature*, 1929, **124**, 762; *Proc. Amsterdam Acad.*, 1930, **33**, 632; *Proc. Roy. Soc.*, 1931, *A*, **127**, 279; Woodward, *Nature*, 1930, **58**, 126; *Physikal. Z.*, 1931, **32**, 212; Kinsey, *Physical Rev.*, 1930, **35**, 284; Dadieu and Kohlrausch, *Naturwiss.*, 1931, **19**, 690; Dadieu, Jele, and Kohlrausch, *Monatsh.*, 1931, **58**, 428; Médard and Volkringer, *Compt. rend.*, 1933, **197**, 833; Médard and Petitpas, *ibid.*, p. 1221; 1934, **198**, 98; Médard, *ibid.*, p. 1407; Aderhold and Weiss, *Z. Physik*, 1934, **88**, 83; Angus and Leckie, *Nature*, 1934, **134**, 572; *Proc. Roy. Soc.*, 1935, *A*, **149**, 327; Susz and Briner, *Helv. Chim. Acta*, 1935, **18**, 379; Venkateswaran, *Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 174; Chédin, *Ann. Chim.*, 1937, **8**, 243; *J. Phys. Radium*, 1939, **10**, 445; Simon and Hoppner, *Kolloid Z.*, 1938, **85**, 8; Chédin and Delmon, *Compt. rend.*, 1939, **209**, 455; Banerji and Mishra, *Indian J. Physics*, 1941, **15**, 359; Mathieu and Massignon, *Compt. rend.*, 1941, **212**, 1084; *Ann. Physique*, 1941, **16**, 5; Redlich and Nielsen, *J. Amer. Chem. Soc.*, 1943, **65**, 654; Chédin and Fénéant, *Mem. Serv. Chim. de l'État*, 1945, **32**, 92).

Measurements of, or qualitative observations on, the polarisation of the Raman lines have been made (in some cases using more or less aqueous nitric acid) by Venkateswaran, by Chédin, and by Mathieu and Massignon (*locc. cit.*). Of the frequencies in the first row of the above list, 680, 925, 1300, and 1535 cm.$^{-1}$ are definitely polarised, whilst 610 and 1675 cm.$^{-1}$ are classified as depolarised. Nothing is known about the state of polarisation of the high-frequency band. The two frequencies in the second row are highly polarised.

The Raman spectrum of deuteronitric acid has been described by Banerji and Mishra, and by Redlich and Nielsen (*locc. cit.*).

The frequencies in the first row of the list given above have been assigned to their vibrations by Chédin, by Mathieu and Massignon, and by Redlich and Nielsen (*locc. cit.*). All three assignments are in large measure correct, but none is entirely complete and correct.

It is agreed that 610 and 680 cm.$^{-1}$ are the two expected ONO-bending frequencies. The former is shown by its depolarisation, and considerable downward shift in deuteronitric acid, to be associated mainly with the bending of $\widehat{ON}$(OH) angles. The latter is equally shown by its polarisation, and lack of substantial shift in deuteronitric acid, to be essentially the symmetric bending frequency of the NO_2 group. The fact that this frequency is the higher suggests that the mesomerism, more fully developed in the NO_2 group than in the ON(OH) groups, tends to stiffen the $O\widehat{N}O$ angle relatively to the $\widehat{ON}$(OH) angles.

It is equally agreed that 925, 1300, and 1675 cm.$^{-1}$ are the three expected ON-stretching frequencies. On account of its value, and the high intensity and polarisation with which it appears, 1300 cm.$^{-1}$ is assumed to be essentially the symmetric stretching frequency of the NO_2 group. The other considerably polarised frequency, 925 cm.$^{-1}$, may be assumed to be associated largely with stretching of the N(OH) bond. These frequencies seem reasonably related, having regard to the mesomeric orders of the bonds. The frequency 1675 cm.$^{-1}$ is shown by its depolarisation to represent a highly dissymmetric mode of motion, evidently antisymmetric stretching in the NO_2 group.

The band at 3400 cm.$^{-1}$ certainly arises from OH-stretching motion. The origin of the line at 1535 cm.$^{-1}$ has never been made clear: this will be discussed below.

Further frequencies have been reported which are less well confirmed than these. A weak frequency, 480 cm.$^{-1}$, has been reported by Redlich and Nielsen, who have attributed it, very reasonably, to out-of-plane hydrogen motion. A frequency near 1110 cm.$^{-1}$ has been reported more than once; nevertheless its existence seems doubtful.

Two further fundamental vibrations of the nitric acid molecule exist, whose frequencies have not yet been identified correctly or with certainty in the Raman spectrum. They are the out-of-plane vibration of the NO_3 group, and the hydrogen-bending vibration involving deformation of the HON angle. Further reference to these vibrations is made below.

(1.2) *Assignment of the Raman Frequency* 1535 *cm.*$^{-1}$.—This line was first assigned by Chédin as the combination tone, $610 + 925 = 1535$ cm.$^{-1}$, simply on the ground that the frequencies agree. However, as Mathieu and Massignon observed, the line is too highly polarised to admit of this interpretation. (A binary combination tone derived from a polarised and a depolarised fundamental frequency should be depolarised.) Furthermore, as Redlich and Nielsen pointed out, the interpretation requires an isotope shift in deuteronitric acid of 40 cm.$^{-1}$, whereas in fact the line is not shifted.

Redlich and Nielsen assigned the line to the fundamental out-of-plane frequency of the NO_3 group. But this seems impossible on the following grounds. First, for the reason explained below, a Raman line representing this fundamental vibration should be *extremely* weak—much weaker, almost certainly, than the line at 1535 cm.$^{-1}$ (cf. Fig. 2). Secondly, such a Raman line should be fully depolarised, whereas the actual line is considerably polarised. Thirdly, the corresponding fundamental frequency of the nitrate ion, with its slightly smaller mass, and considerably more fully developed mesomerism, is only 830 cm.$^{-1}$, as is known from the infra-red study of nitrates. The analogous frequency of the nitric acid molecule could hardly be greater than this, and, essentially on account of the diminished mesomerism, would be expected to be somewhat smaller.

The frequency 1535 cm.$^{-1}$ is now assigned as the first overtone of the out-of-plane vibration of the NO_3 group. The corresponding fundamental frequency, 770 cm.$^{-1}$ according to this interpretation, is not likely to be visible in the Raman spectrum, even though it is not forbidden by symmetry; for in the nitrate ion, the corresponding fundamental frequency is forbidden by symmetry in the Raman effect, and all that makes this type of vibration in the nitric acid molecule allowed in principle is the possibility of coupling between this motion and the restricted rotation of the hydrogen atom. However, any such coupling must be extremely weak. It is therefore intrinsically likely that the out-of-plane vibration of the NO_3 group of the nitric acid molecule will be represented in the Raman spectrum considerably more strongly by its first overtone than by its " practically forbidden " fundamental frequency; for the first overtone, though limited as to amplitude by the anharmonicity of the vibration, is of the right symmetry for a strong appearance in the Raman spectrum.

The same spectral properties of this line at 1535 cm.$^{-1}$, which disprove the former interpretations, confirm this one. For first, the vibrational wave-function being totally symmetrical, not only with respect to the whole molecule, but also with respect to the NO_3 group, the Raman line should be considerably polarised. Secondly, since there can be no appreciable coupling between the out-of-plane NO_3 motion and out-of-plane hydrogen motion, neither the fundamental frequency nor its first overtone should show any isotope shift when the mass of the hydrogen atom is changed.

(1.3) *Assignment of the Infra-red Frequency* 780 *cm.*$^{-1}$.—The infra-red spectrum of nitric acid has been observed over the range 6—15 μ. by Freymann and Freymann (*Compt. rend.*, 1946, **222**, 1339). They report bands corresponding to all the main Raman lines falling within this spectral range, together with one further band in the region 770—790 cm.$^{-1}$. Very tentatively they suggested that this might be the fundamental band of the out-of-plane NO_3 vibration. The arguments of the preceding section show that these authors' suggestion is almost certainly correct.

It can be predicted that the corresponding infra-red frequency of deuteronitric acid will also be found at 780 cm.$^{-1}$.

(1.4) *The Hydrogen-bending Vibration.*—For the purpose of assigning a frequency to this vibration, Redlich and Nielsen assumed the Raman line at 1675 cm.$^{-1}$ to be double; but experimentally they could find no sign of doubling, and that is also the experience of the present authors (cf. Fig. 2).

As the hydrogen-bending frequency of deuteronitric acid, Redlich and Nielsen offer a frequency of about 1340 cm.$^{-1}$, represented by a bulge on the high-frequency flank of the contour of the strong line near 1300 cm.$^{-1}$. It has been found in the course of the present experiments that the contour of the line at 1300 cm.$^{-1}$ of ordinary nitric acid likewise contains a bulge on the high-frequency side (cf. Fig. 2). The frequency responsible for this bulge is estimated as about 1360 cm.$^{-1}$. It is obviously possible that these frequencies, neither of which can be determined accurately, have a common origin in the first overtone of the $\widehat{ONO}$-bending vibration, whose fundamental frequency is 680 cm.$^{-1}$ in ordinary nitric acid, and is only slightly reduced in deuteronitric acid.

Owing to the largely ionic character of the OH-bond of nitric acid, the hydrogen-bending frequency is expected to be extremely weak in the Raman effect, probably unobservably weak under the conditions of the present experiments, just as the frequency due to the restricted rotation of the hydrogen atom is unobservably weak. Certainly all the frequencies which have been observed in the course of the present experiments can be understood without appealing to either of these vibrations, whose frequencies will be sought in the infra-red spectrum, where they should appear strongly.

(1.5) *The Breadth of the Raman Lines.*—The great breadth of the hydrogen-stretching Raman band near 3400 cm.$^{-1}$ undoubtedly arises from the intermolecular hydrogen-bonding in liquid nitric acid, as Chédin and Fénéant have pointed out already (*loc. cit.*). Hydrogen-bonding should also cause the hydrogen-bending frequency, and the restricted-rotational hydrogen frequency, to be represented by diffuse bands in the Raman spectrum of liquid nitric acid; their small total intensity being thus smeared out, this may be another reason why we have not observed them.

Most of the other Raman frequencies of liquid nitric acid, though not as broad as the high-frequency band, are still remarkably broad. Thus, in some of our photographs, the total contour of the line having its intensity maximum near 1300 cm.$^{-1}$ extends over about 250 cm.$^{-1}$. Obviously this strong line could obscure a very weak one at distances up to 100 cm.$^{-1}$ away from its intensity maximum, unless the weak line were particularly sharp. This limitation which the breadth of the strong lines imposes on the observation of neighbouring weak ones is of importance for the understanding of the self-ionisation spectrum of nitric acid. No doubt the cause of the unusual breadth of the Raman lines of nitric acid is, once again, intermolecular hydrogen-bonding.

(2) *Raman Spectra of Mixtures of Nitric Acid and Water.*

(2.1) *General Effects of Added Water on the Nitric Acid Spectrum.*—One of the first effects on the Raman spectrum of nitric acid of the progressive addition of water to the nitric acid is the suppression of the self-ionisation spectrum, which is to be considered in Section 4. Another early effect of added water is to change the forms of hydrogen-bonding doubtless through the production of a hydrogen-bonded hydrate of nitric acid, and thus to produce modifications in the high-frequency band of nitric acid, as has been shown in detail by Chédin and Fénéant (*loc. cit.*). Further amounts of water produce nitrate ion; and we shall be concerned in Sections 3 and 4 with the appearance of the Raman spectrum of the nitrate ion in the presence of a large excess of molecular nitric acid.

(2.2) *The Raman Frequencies of the Nitrate Ion.*—Only the three planar vibrations of the nitrate ion, one totally symmetrical and two doubly degenerate, are allowed to record their fundamental frequencies in the Raman spectrum. The single out-of-plane vibration is forbidden as a fundamental, though its first overtone is allowed.

The literature contains a number of records of the Raman spectra of mixtures of nitric acid and water. Difficulties attended the first attempts to identify the nitrate ion frequencies, although it was agreed by Rao, Kinsey, and Woodward that 1050 cm.$^{-1}$ was one of them. The other allowed fundamental frequencies were found, first in solutions of nitrates by Ramaswarmy and then in aqueous nitric acid by Brunetti and Ollando; in cm.$^{-1}$ they are as follows:

720 (w) 1050 (s) 1360 (w)

(Carelli, Prungsheim, and Rosen, *Z. Physik*, 1928, **51**, 511; Ganesan and Venkateswaran, *Indian J. Physics*, 1929, **4**, 196; Schaefer, Matossi, and Aderhold, *Physikal. Z.*, 1929, **30**, 581; *Z. Physik*, 1930, **65**, 301; Rao, *loc. cit.*; Kinsey, *loc. cit.*; Woodward, *loc. cit.*; Ramaswarmy, *Indian J. Physics*, 1930, **5**, 193; Brunetti and Ollando, *Atti Accad. Lincei*, 1931, **13**, 52; Médard and Petitpas, *Compt. rend.*, 1933, **197**, 1221; Venkateswaran, *Phil. Mag.*, 1933, **15**, 263; *Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 174; Chédin, *Ann. Chim.*, 1937, **8**, 284; Kujumzelis, *Z. Physik*, 1938, **109**, 586; Redlich and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 1883).

Venkateswaran found the strong line at 1050 cm.$^{-1}$ to be highly polarised, a result which proves that it belongs to the totally symmetrical vibration of the ion. He found the two weak lines to be depolarised, and this shows that they belong to the degenerate bending, and degenerate stretching, vibrations of the nitrate ion.

The Raman line at 1050 cm.$^{-1}$, because it is strong and well separated from any Raman frequency of molecular nitric acid, is a good index of nitrate ion concentration. On the contrary, not only are the other two active fundamentals, 720 and 1360 cm.$^{-1}$, quite weak, but also the upper one is broad, and each lies fairly close to an important frequency of the nitric acid molecule. These nitric acid frequencies, 680 and 1300 cm.$^{-1}$, are strong and broad; and therefore each overlaps the nitrate ion frequency in its neighbourhood.

Reference may be made to some additional nitrate ion frequencies, which have been observed by the use of crystalline nitrates. The out-of-plane fundamental of the nitrate ion, though forbidden in the Raman effect, is allowed in the infra-red spectrum; and it has been observed as a band at 831 cm.$^{-1}$ in the infra-red spectrum of crystalline sodium nitrate (Schaefer and Schubert, *Ann. Physik*, 1918, **55**, 577). In the Raman spectrum of the same substance, there have been observed the three planar fundamental frequencies of the nitrate ion, some quite low frequencies belonging to lattice vibrations, and one additional, very weak frequency, 1665 cm.$^{-1}$ (Krishnamurti, *Indian J. Physics*, 1930, **5**, 1; Schaefer, Matossi, and Aderhold, *Z. Physik*, 1930, **65**, 289). There can be little doubt that this last frequency is the allowed first overtone of the out-of-plane vibration of the nitrate ion.

(3) *Raman Spectra of Mixtures of Nitric Acid and Dinitrogen Pentoxide.*

(3.1) *Ionisation of Dinitrogen Pentoxide.*—The Raman spectra of solutions of dinitrogen pentoxide in nitric acid have been described by Briner and Susz (*Helv. Chim. Acta*, 1935, **18**, 378), and by Chédin (*Compt. rend.*, 1935, **200**, 1397; *Ann. Chim.*, 1937, **8**, 243). It is agreed, and is confirmed in the present work, that the spectrum contains all the lines of molecular nitric acid, and in addition two lines, having the frequencies 1050 and 1400 cm.$^{-1}$, and intensities which are approximately proportional to the concentration of dinitrogen pentoxide. Chédin observed, and it is here confirmed, that the spectrum does not contain any of the Raman frequencies of molecular dinitrogen pentoxide, several of which, *viz.* (in cm.$^{-1}$),

860 (w) 1244 (ms) 1335 (s, sharp)

are diagnostically serviceable, as was proved by observations on the Raman spectra of dinitrogen pentoxide in neutral solvents (Chédin, *Compt. rend.*, 1935, **201**, 552; Chédin and Pradier, *ibid.*, 1936, **203**, 772; cf. Chédin, *Ann. Chim.*, 1937, **8**, 243).

The Raman line at 1400 cm.$^{-1}$ has been identified as the totally symmetrical fundamental of the nitronium ion (Part I, *J.*, 1950, 2576). We know that the strongest Raman frequency of the nitrate ion lies at 1050 cm.$^{-1}$ (Section 2.2), and it will be shown below (Section 3.2) that the line found at this frequency along with the line at 1400 cm.$^{-1}$, in the spectra of solutions of dinitrogen pentoxide in nitric acid, in fact belongs to the nitrate ion. The formation of the two ions may be represented thus :

$$N_2O_5 = NO_2^+ + NO_3^-$$

The complete absence from the relevant spectra of lines due to molecular dinitrogen pentoxide shows that this electrolytic dissociation is quantitative.

(3.2) *Identification of the Nitrate Ion.*—It will now be shown that all the appearances that are to be expected from the presence of the nitrate ion are found in the Raman spectrum of a solution of dinitrogen pentoxide in nitric acid.

For this purpose it is convenient to compare the Raman spectrum of a solution of dinitrogen pentoxide in nitric acid with that of a solution of ammonium nitrate in nitric acid. Table I records some frequency displacements measured in Raman spectra of solutions of these types, as well as in the Raman spectrum of anhydrous nitric acid, the measurements relating to Stokes lines excited by nitrite-filtered Hg 4358 A. The assignment of the lines is indicated in Table I, partly in anticipation of the following discussion.

TABLE I.

Raman frequencies of (*i*) *anhydrous nitric Acid,* (*ii*) *a solution,* 6% *by weight, of dinitrogen pentoxide in nitric acid, and* (*iii*) *a solution,* 15% *by weight, of ammonium nitrate in nitric acid.*

(Frequency separations in cm.$^{-1}$ from Hg 4358 A.)

Assignments to HNO_3.	(i) HNO_3.		(ii) N_2O_5 in HNO_3.		(iii) NH_4NO_3 in HNO_3.		Assignments to ions.
Fundamental	609	ms	609	ms	620	ms	—
Fundamental	677	ms	677	ms	680	ms	—
	—	—	(720) *	vw	720	w	NO_3^-
Fundamental	925	s	929	s	929	s	—
	1049	w	1052	m	1048	s	NO_3^-
Funadmental	1296	vs	1298	vs	1303	vs	—
Overtone †	(1360) *	vw	(1360) *	vw	—	—	(NO_3^-) †
	1392	w	1396	m	—	—	NO_2^+
Overtone	1533	w	1540	w	1540	w	—
Fundamental	1670	m	1677	m	1672	m	—

* Roughly estimated, unresolved frequencies are given in parentheses.

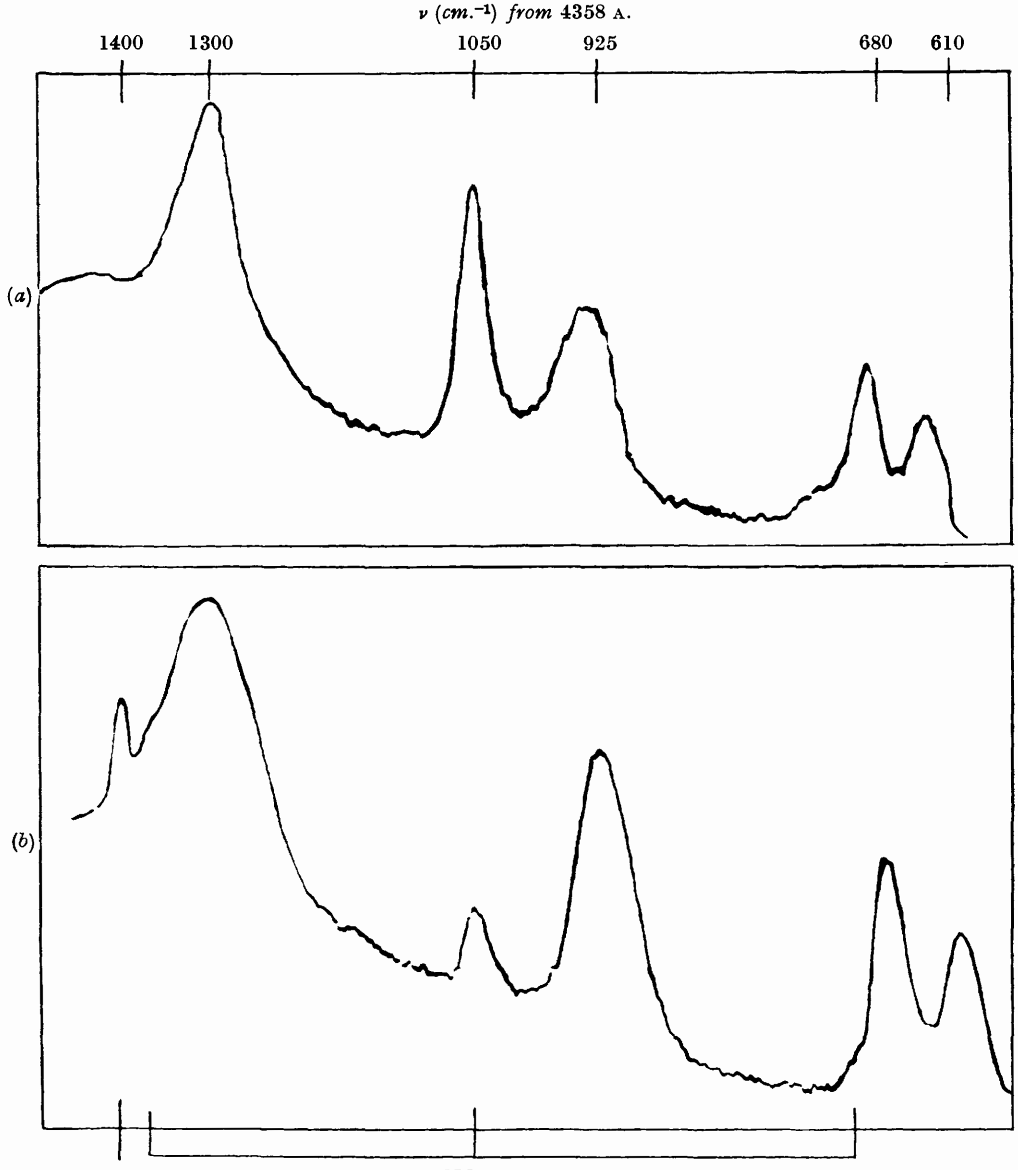
† Part of the intensity of frequency 1360 cm.$^{-1}$ will be due to nitrate ion, and part to the overtone in the nitric acid spectrum.

It is convenient to consider first the spectrum of the solution of ammonium nitrate, a microphotometer record of part of which is shown in Fig. 1*a*. In this spectrum we see, in addition to nitric acid lines, two of the three Raman fundamentals of the nitrate ion. The totally symmetrical frequency, 1050 cm.$^{-1}$, is strongly developed. The bending frequency, 720 cm.$^{-1}$, is apparent as a just-resolved step-out from the contour of the nitric acid frequency 680 cm.$^{-1}$. The non-totally symmetrical stretching frequency of the nitrate ion, 1360 cm.$^{-1}$, is in any case useless for diagnostic purposes in the presence of nitric acid, because it is overlapped by a nitric acid overtone frequency; and in this particular solution both these frequencies are overlaid by a diffuse band due to the degenerate bending frequencies of the ammonium ion.

Let us now compare these results with those obtained for the solution of dinitrogen pentoxide, a microphotometric record of part of the spectrum of which is reproduced in Fig. 1*b*. Here we find nitric acid lines, and the nitronium ion line at 1400 cm.$^{-1}$, together with certain appearances

FIG. 1.

Microphotometer records of parts of the Raman spectra, excited by Hg 4358 A. *filtered through nitrite, of* (a) *a solution,* 15% *by weight, of ammonium nitrate in anhydrous nitric acid, and* (b) *a solution,* 6% *by weight, of dinitrogen pentoxide in anhydrous nitric acid.*



(*a*) 15% NH_4NO_3 *in* HNO_3. (*b*) 6% N_2O_5 *in* HNO_3.

clearly due to the nitrate ion. The breathing frequency, 1050 cm.$^{-1}$, is prominent, though weaker than before, because of the smaller concentration of nitrate ion. For the same reason, the bending frequency, 720 cm.$^{-1}$, though easily visible, is now weaker, appearing only as an unresolved step-out from the contour of the nitric acid line at 680 cm.$^{-1}$. The third nitrate ion fundamental, 1360 cm.$^{-1}$, in combination with the nitric acid overtone estimated to have about the same frequency, may be considered jointly responsible for the bulge which can be seen on the contour of the nitric acid line at 1300 cm.$^{-1}$, just above the extruding nitronium ion line at

1400 cm.$^{-1}$. Thus all the appearances which the nitrate ion would be expected to produce are found in this spectrum.

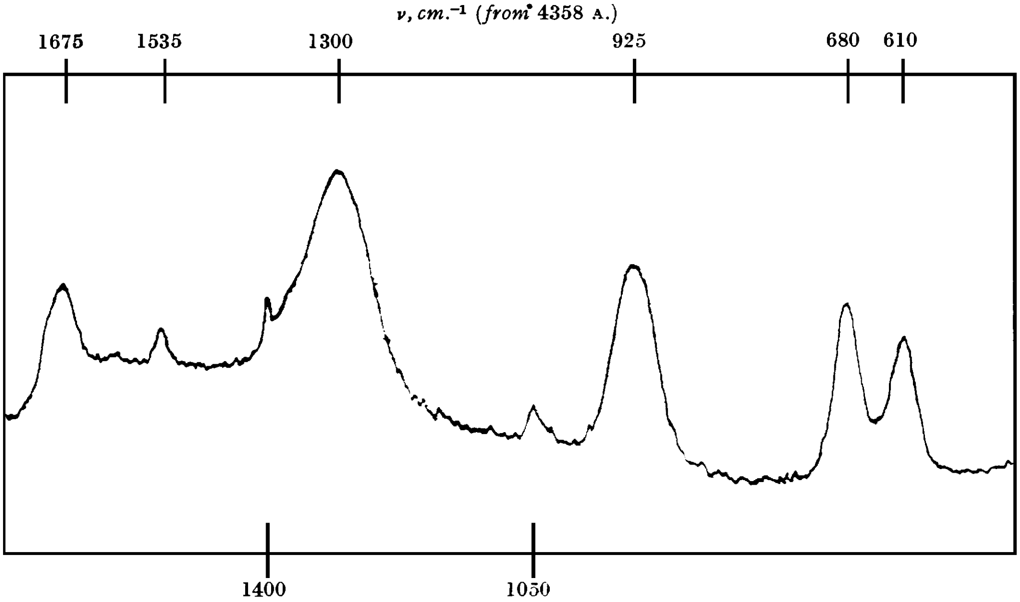
(4) *Raman Spectrum of the Self-ionisation of Nitric Acid.*

(4.1) *The Self-ionisation of Nitric Acid.*—In Section 1 an interpretation of the observed Raman spectrum of nitric acid was offered, which was complete except in regard to the two frequencies, 1400 and 1050 cm.$^{-1}$, both of which appear with low intensity in the spectrum of absolute nitric acid. A microphotometer record of part of this spectrum is reproduced in Fig. 2, in which the two lines mentioned can be clearly seen.

The line at 1400 cm.$^{-1}$ has already been recognised as diagnostic of the nitronium ion (Part I, *J.*, 1950, 2576). The line at 1050 cm.$^{-1}$ is identified as belonging to the nitrate ion, in part by comparison with the nitrate ion line of this frequency shown in Fig. 1*b*. Furthermore, the line at 1050 cm.$^{-1}$ constitutes the only appearance in the spectrum of the anhydrous acid which nitrate ions in the indicated concentration would be expected to produce : we could not expect clearly to observe the step-out at 720 cm.$^{-1}$; and the visible weak frequency at 1360 cm.$^{-1}$ agrees, as has been mentioned earlier, with an allowed overtone frequency of nitric acid.

FIG. 2.

Microphotometer record of part of the Raman spectrum of absolute nitric acid. (Molecular frequencies are noted above the photograph, and self-ionisation frequenices below.)



Thus the two frequencies, 1400 and 1050 cm.$^{-1}$, constitute the observed Raman spectrum of the products of the self-ionisation of nitric acid, according to the equation

$$2HNO_3 = NO_2^+ + NO_3^- + H_2O$$

(which neglects the solvation by nitric acid of the products of its self-ionisation). The extent of this self-ionisation can in principle be determined from the intensities of the relevant lines, but with such weak lines the measurement is only approximate. It is thus estimated that anhydrous nitric acid contains about 1·0% by weight of nitronium ion and 1·5% by weight of nitrate ion, either value being subject to a possible error of 20%. Assuming the above equation to be accurate, and allowing for the water involved, these figures mean that about 3% of anhydrous nitric acid is self-dissociated.

These values may be compared with Gillespie, Hughes, and Ingold's estimate (*J.*, 1950, 2552), based on the rounding of the freezing-point maximum of the system N_2O_5–H_2O at the composition HNO_3, of the total concentration of all self-dissociation products in anhydrous nitric acid. For this total they obtain the value 0·82 molal, which corresponds, if the above equation is accurate, to nitronium ion, nitrate ion, and water, each in 0·27 molal concentration. Spectroscopically, we find 0·22 molal nitronium ion, and 0·24 molal nitrate ion.

These spectroscopic determinations establish that the above-written ionic self-dehydration is the principal mode of self-dissociation of nitric acid. The alternative is auto-protolysis,

$$2HNO_3 = H_2NO_3^+ + NO_3^-$$

and this reaction may indeed take place. But it cannot be the chief form of dissociation, because the nitronium ion and nitrate ion are in approximate equivalence. Essentially, absolute nitric acid is to be regarded as a dilute (~ molal/4) solution, in nitric acid, of dinitrogen pentoxide and water (cf. Norman Jones, Thorn, Lyne, and Taylor, *Nature*, 1947, **159**, 163; Jones and Thorn, *Canadian J. Res.*, 1949, *B*, **27**, 580).*

(4.2) *Suppression of the Self-ionisation of Nitric Acid.*—One part of the spectroscopic demonstration that the self-ionisation process represented above is reversed by the addition of each of its products has been supplied by Chédin, who has found that the addition of about 1·5% of water to anhydrous nitric acid suffices to render the nitronium ion line unobservably weak in the Raman spectrum (*Ann. Chim.*, 1937, **8**, 243; and personal communication). In the course of the present experiments, this type of confirmation of the presumed equilibrium has been completed, by showing that the addition of nitronium perchlorate destroys the nitrate ion line, whilst the addition of ammonium nitrate destroys the nitronium ion line. The types of spectra which may be obtained by these means are sufficiently illustrated by Fig. 1*a* of Part I, and Fig. 1*a* of this paper.

According to the above estimate of ion concentrations, based on intensities in the self-ionisation spectrum, "anhydrous" nitric acid should contain about 0·4% by weight of water (doubtless present as a nitric acid hydrate). The amount of added water which is necessary to render the ionic lines unobservably weak must obviously be several times greater than this, and accordingly the figure 1·5% give by Chédin seems consistent. A similar check can be obtained by reference to the electrical conductivity of nitric acid; for evidently the amount of added water necessary to bring the conductivity to a minimum must be several times greater than the amount of water in the anhydrous acid, because it has to suppress the self-ionisation almost completely, and has also just to start the aqueous ionisation of nitric acid. The amount necessary is 3% (cf. *J.*, 1950, 2422), and this also seems consistent with the spectral and cryoscopic evidence. A similar rough check is provided by the thermochemical work of Chédin, Leclerc, and Vandoni (*Compt. rend.*, 1947, **225**, 734), who have shown that the exothermicity of addition of water to a large excess of nitric acid is maximal for slightly aqueous acid. It is relatively small for anhydrous acid (and still smaller for acid containing an excess of dinitrogen pentoxide), because the water has to endothermically desolvate the nitronium and nitrate ions before it can hydrate the dinitrogen pentoxide. In highly aqueous acid, the exothermicity of water addition is again diminished, obviously because the previously present water will reduce the solvation by nitric acid of the newly added water. The endothermic maximum separating those two effects will evidently be attained when the amount of water added is enough to suppress nearly all the self-dissociation of the nitric acid but is not enough to reduce by much the degree of solvation of the added water. The amount of water will therefore be several times greater than 0·4%, but still only a small mol.-fraction (*i.e.*, a few units %). The endothermic maximum is found with acid containing 2·5% of water, and this again seems consistent with the other kinds of evidence mentioned.

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* Since dinitrogen pentoxide is completely ionised in the solid state (Ingold, Millen, and Poole, *Nature*, 1946, **158**, 480; see also preceding paper), and is likewise completely ionised in dilute solution in nitric acid (Gillespie, Hughes, and Ingold, *J.*, 1950, 2552; Section 3 of this paper), it is just as true to say that a solution prepared by dissolving dinitrogen pentoxide in nitric acid *contains* dinitrogen pentoxide, as that a solution of sodium chloride in water contains sodium chloride: for in either case, when the solid dissolves, the ions fall apart without covalency change. Generally, any solution, which contains nitronium and nitrate ions, contains dinitrogen pentoxide, which (as ordinarily seen and preserved) is an ionic substance. Thus Briner and Susz were correct when they ascribed to dinitrogen pentoxide the Raman frequencies 1400 and 1050 cm.$^{-1}$, observed in the spectrum of nitric oleum, as was Chédin when he similarly assigned the same frequencies, found in the spectrum of anhydrous nitric acid. Berl was likewise correct in assuming the solvation of dinitrogen pentoxide by nitric acid in explanation of the vapour pressures of his solutions. These remarks are made in qualification of Bennett, Brand, and Williams's criticism of what they call "the nitrogen pentoxide hypothesis" (*J.*, 1946, 874).