508. Vibrational Spectra of Ionic Forms of Oxides and Oxy-acids of Nitrogen. Part III. Raman Spectral Evidence of the Ionisation of Dinitrogen Trioxide, Dinitrogen Tetroxide, and Dinitrogen Pentoxide by Sulphuric Acid.

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Raman spectra of solutions of dinitrogen trioxide in sulphuric acid indicate that the following reaction takes place completely, slight incompleteness of the ionisation of water being neglected:

$$N_2O_3 + 3H_2SO_4 = 2NO^+ + 3HSO_4^- + H_3O^+ \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

A quantity of added water that would be enough completely to destroy nitronium ion by converting it (cf. Part I, Section 4) into molecular nitric acid in reaction (3), is insufficient to convert a detectable amount of nitrosonium ion at identical concentrations in the analogous reaction (2):

$$NO^+ + 2HSO_4^- + H_3O^+ = HNO_2 + 2H_2SO_4 \quad . \; . \; . \; . \; . \quad (2)$$

$$NO_2^+ + 2HSO_4^- + H_3O^+ = HNO_3 + 2H_2SO_4 \quad . \; . \; . \; . \; . \quad (3)$$

Thus, in thermodynamic comparison, the nitrosonium ion has a much smaller electrophilic reactivity towards water than has the nitronium ion.

Raman spectra of solutions of dinitrogen tetroxide in sulphuric acid show that, in dilute solution, the following reaction is quantitative except for the incompleteness of water ionisation:

$$N_2O_4 + 3H_2SO_4 = NO^+ + NO_2^+ + 3HSO_4^- + H_3O^+ \quad . \; . \; . \; . \quad (4)$$

In more concentrated solution, the build-up of nitronium ion, and of the ions of water, by reaction (4) can be sufficient to allow the nitronium ion to show its thermodynamic instability by reacting with the water ions to form an appreciable amount of molecular nitric acid in the balanced process (3). Nothing analogous happens to the simultaneously formed nitrosonium ions, within the range of concentrations studied.

Raman spectra of solutions of dinitrogen pentoxide in sulphuric acid prove that, in dilute solution, the following reaction takes place quantitatively, apart from water ionisation:

$$N_2O_5 + 3H_2SO_4 = 2NO_2^+ + 3HSO_4^- + H_3O^+ \quad . \; . \; . \; . \; . \quad (5)$$

In more concentrated solutions of dinitrogen pentoxide in sulphuric acid, the build-up of nitronium ions, and of the ions of water, by reaction (5) can again lead to appreciable production of molecular nitric acid by the balanced process (3). Thus the two reactions together constitute a hydration–dehydration disproportionation of dinitrogen pentoxide.

(1) *Ionisation of Dinitrogen Trioxide in Sulphuric Acid.*

(1.1) *Raman-spectroscopic Properties of Nitrosonium Salts.*—A brief consideration of this subject is a necessary preliminary to the investigation of some of the Raman spectra described below.

Nitrosonium hydrogen sulphate has long been known as " chamber crystals " or " nitrosylsulphuric acid," and several non-ionic structures have been proposed for it. Hantzsch and Berger (*Z. anorg. Chem.*, 1930, **190**, 321) first showed that it behaved as a binary electrolyte in sulphuric acid. They also brought forward evidence, based on its reactivity, that the ions are nitrosonium and hydrogen sulphate ions. They suggested that the solid compound had the ionic structure $(NO^+)(HSO_4^-)$, and proposed similar structures for other nitrosonium salts, such as the perchlorate and fluoroborate.

The Raman spectra of solid nitrosonium hydrogen sulphate, and of its solutions in sulphuric acid (Angus and Leckie, *Proc. Roy. Soc.*, 1935, **149**, 327), are all characterised by a line at approximately 2320 cm.$^{-1}$. The interpretation of these spectra is not entirely unambiguous, because of the presence of a number of other lines, whose origin is not clear. The interpretation of the Raman spectrum of nitrosonium perchlorate (Angus and Leckie, *Proc. Roy. Soc.*, 1935, *A*, **150**, 615) is, however, unequivocal. The frequencies of the solid, and of its solutions in aqueous perchloric acid of two concentrations, together with the well-established frequencies of the perchlorate ion (Redlich, Holt, and Bigeleisen, *J. Amer. Chem. Soc.*, 1944, **66**, 13), are quoted in Table I.

TABLE I.

Raman frequencies (in cm.$^{-1}$) of nitrosonium perchlorate (after Angus and Leckie).

Solid.	Solution in 62 wt. % $HClO_4$.	Solution in 48 wt. % $HClO_4$.	Perchlorate ion.
463 (m)	469 (ms)	450 (w)	464 (m)
703 (m)	633 (ms)	623 (m)	631 (ms)
929 (ms)	932 (ms)	930 (vs)	940 (vs)
1117 (vw)	1113 (vw)	1106 (w)	1053—1167 (w. band)
2329 (s)	2319 (m)	2313 (vw)	—

Of the five frequencies which appear in each spectrum of nitrosonium perchlorate, four may be assigned to the perchlorate ion, although, in the case of the solid, the frequency of the doubly degenerate bending vibration is considerably displaced. The fifth frequency, 2320 cm.$^{-1}$, is assigned as the fundamental frequency of the nitrosonium ion, NO^+, and this is supported by comparison with the isoelectronic molecule, N_2, which has its fundamental frequency at 2330 cm.$^{-1}$. The appearance of a line at 2320 cm.$^{-1}$ in the spectra of solutions of both nitrosonium hydrogen sulphate and the perchlorate demonstrates that the frequency is nearly independent of the remainder of the molecule, and this is consistent with its assignment to a common ion.

(1.2) *Raman Spectra of Solutions of Dinitrogen Trioxide in Sulphuric Acid.*—In Table II the frequencies belonging to three Raman spectra are given. Column 1 contains the frequencies of pure sulphuric acid (Part I, *J.*, 1950, 2576), column 2 the frequencies found in the spectrum of a mixture of 10 mols. of dinitrogen trioxide with 90 mols. of sulphuric acid, and column 3 the frequencies found in the spectrum of a solution of dinitrogen trioxide in aqueous sulphuric acid. The frequencies near 2300 cm.$^{-1}$ were measured as Raman displacements of Stokes lines excited by Hg 4047 A., an iodine filter being used. In the spectrum of the solution in anhydrous sulphuric acid, a Raman frequency of 2307·7 cm.$^{-1}$, excited as a Stokes line by Hg 4078 A., was also found. The remaining frequencies refer to measurements of Stokes lines excited by nitrite-filtered Hg 4358 A.

TABLE II.

Raman frequencies (in cm.$^{-1}$) of solutions of dinitrogen trioxide in sulphuric acid.

Pure H_2SO_4.	Solutions of N_2O_3 in (i) anhydr. H_2SO_4.	(ii) aq. H_2SO_4.	Pure H_2SO_4.	Solutions of N_2O_3 in (i) anhydr. H_2SO_4.	(ii) aq. H_2SO_4.
391 (ms)	408 (m)	418 (m)	—	1043 (s)	1034 (vs)
416 (ms)			1125—1195 (s)	1172 (s)	1191 (ms)
562 (s)	561 (ms)	574 (m)	1376 (mw)	1372 (mw)	—
912 (s)	902 (s)	903 (m)	—	1398 (vw)	—
976 (w)	—	—	—	2307·9 (s)	2290 (m)

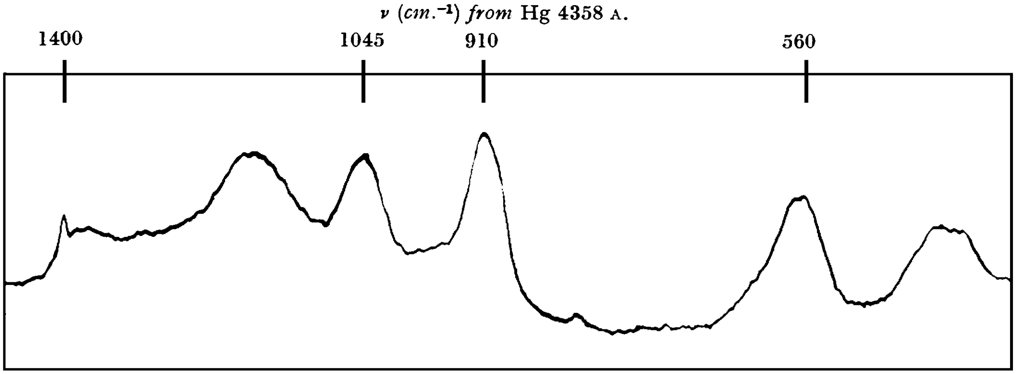
The spectrum of the solution in anhydrous sulphuric acid contains all the lines of the sulphuric acid molecule, except the weak one at 976 cm.$^{-1}$; and it contains three other lines, having the frequencies 1043, 1398, and 2307·9 cm.$^{-1}$. Two of these appear in the microphotometer record reproduced in Fig. 1.

The weak frequency 1398 cm.$^{-1}$ has no significance for the ionisation of dinitrogen trioxide by sulphuric acid: it belongs to the nitronium ion. This is present as an impurity, because the heat of mixing of dinitrogen trioxide with sulphuric acid renders it difficult to prepare a mixture (cf. Gillespie *et al.*, *J.*, 1950, 2504) without causing some loss of nitric oxide, with an accompanying formation of dinitrogen tetroxide, which is the source of the nitronium ion (cf. Section 2.2). Of the remaining frequencies, 2308 cm.$^{-1}$ and 1043 cm.$^{-1}$, the former can only be the fundamental frequency of the nitrosonium ion, whilst the latter is assigned to the hydrogen sulphate ion.

In support of this assignment of the line at 1040 cm.$^{-1}$, it may be pointed out that its contour matches that of the corresponding line in the spectrum of aqueous sulphuric acid (cf. Fig. 2*b* of Part I), and that those other appearances which are to be expected from the presence of the hydrogen sulphate ion are found in the spectrum. These appearances are (cf. Part I) a marked thickening and dissymmetry of the sulphuric acid line at 560 cm.$^{-1}$ in the direction of a satellite at about 590 cm.$^{-1}$, and a similar, but much smaller, deformation of the sulphuric acid line at 910 cm.$^{-1}$ in the direction of a satellite at about 895 cm.$^{-1}$ (cf. Fig. 1).

FIG. 1.

Microphotometer record of part of the Raman spectrum of a mixture of 10 *mols. of dinitrogen trioxide with* 90 *mols. of sulphuric acid.*



The spectrum of the mixture of dinitrogen trioxide and sulphuric acid is thus fully explained by assuming complete ionisation to nitrosonium ion and hydrogen sulphate ion :

$$3H_2SO_4 + N_2O_3 = 2NO^+ + 3HSO_4^- + H_3O^+$$

This equation is approximate inasmuch as it neglects the incomplete ionisation of water by sulphuric acid (Gillespie, *J.*, 1950, 2493).

It is convenient to consider the solution of dinitrogen trioxide in aqueous sulphuric acid as a mixture belonging to the system H_2SO_4–HNO_2–H_2O, and to compare its spectrum with that of the corresponding mixture of the system H_2SO_4–HNO_3–H_2O. The composition of the former system, calculated on this basis, is 43 mols. H_2SO_4, 10 mols. HNO_2, 47 mols. H_2O. The corresponding mixture in which nitric acid replaces nitrous acid contains just sufficient water to destroy all the nitronium ion (Chédin, *Ann. Chim.*, 1937, **8**, 303; Gillespie and Millen, *Quart. Reviews*, 1948, **2**, 285); and so the frequency 1400 cm.$^{-1}$ is absent from its spectrum, whilst the frequencies of molecular nitric acid are strongly developed (cf. Part I, Section 4, *J.*, 1950, 2576).

The spectrum of the mixture derived from dinitrogen trioxide shows all the characteristics of the hydrogen sulphate ion spectrum, as well as a moderately strong nitrosonium ion line near 2300 cm.$^{-1}$. Thus the spectrum can be completely understood as that of a solution of nitrosonium and hydrogen sulphate ions in sulphuric acid. There are no lines which could be attributed to an oxy-acid of nitrogen, although it is possible that weak lines might have been obscured. However, it is clear that nitrous acid exists very largely in the cationic form, NO^+, in this solution, and that nitric and nitrous acids behave in entirely different ways in the two mixtures of corresponding composition. We conclude that the equilibrium constant for the following ionisation of nitrous acid by sulphuric acid,

$$HNO_2 + 2H_2SO_4 = NO^+ + 2HSO_4^- + H_3O^+$$

is much greater than that for the corresponding ionisation of nitric acid by sulphuric acid, *viz.*,

$$HNO_3 + 2H_2SO_4 = NO_2^+ + 2HSO_4^- + H_3O^+$$

The larger negative Gibbs free-energy of formation of nitric acid than of nitrous acid, and the reverse order of thermodynamic stability of the corresponding cations both contribute to this difference in the equilibrium constants.

(2) *Ionisation of Dinitrogen Tetroxide in Sulphuric Acid.*

(2.1) *The Condition of Dinitrogen Tetroxide in Sulphuric Acid.*—It has been shown that solutions of dinitrogen tetroxide in sulphuric acid are capable of nitrating aromatic compounds (Pinck, *J. Amer. Chem. Soc.*, 1927, **49**, 2536). Only one nitro-group is introduced into the aromatic compound for each molecule of dinitrogen tetroxide used. If it is assumed that the effective nitrating agent in the solution is the nitronium ion, then these results are consistent with the assumption of an ionisation of dinitrogen tetroxide by sulphuric acid according to the following equation :

$$N_2O_4 + 3H_2SO_4 = NO_2^+ + NO^+ + 3HSO_4^- + H_3O^+$$

Cryoscopic examination of the solution (Gillespie *et al.*, *J.*, 1950, 2504) has yielded results which are in agreement with this equation, when a small allowance is made for the incomplete ionisation of water by sulphuric acid.

(2.2) *Raman Spectra of Solutions of Dinitrogen Tetroxide in Sulphuric Acid.*—In Table III are recorded the results of frequency measurements (cm.$^{-1}$) made upon the Raman spectra of (i) anhydrous sulphuric acid, (ii) a mixture of 10 mols. of dinitrogen tetroxide with 90 mols. of sulphuric acid, and (iii) a mixture of 20 mols. of dinitrogen tetroxide with 80 mols. of sulphuric acid. The frequencies of approximately 2300 cm.$^{-1}$ were measured as Raman displacements of Stokes lines excited by Hg 4047 A., simultaneous excitation by Hg 4358 A. being excluded by means of an iodine filter. The same frequencies were also measured as displacements, by 2302 cm.$^{-1}$, from Hg 4078 A. in the spectrum of each of the dinitrogen tetroxide solutions. The remaining frequencies refer to measurements of Stokes lines excited by nitrite-filtered Hg 4358 A.

TABLE III.

Raman frequencies (*in cm.*$^{-1}$) *of solutions of dinitrogen tetroxide in sulphuric acid.*

Pure H_2SO_4.	N_2O_4 (10 mols.) $+H_2SO_4$ (90 mols.).	N_2O_4 (20 mols.) $+H_2SO_4$ (80 mols.).
391 (ms) 416 (ms)	415 (ms)	412 (ms)
562 (ms)	565 (ms)	565 (ms)
—	—	680 (vw)
912 (s)	903 (s)	905 (s)
976 (w)	—	—
—	1046 (s)	1042 (s)
1125—1195 (s)	1179 (s)	1181 (s)
—	—	1313 (w)
1376 (mw)	—	—
—	1404 (s)	1400 (s)
—	—	1670 (vw)
—	2303 (s)	2301 (s)

The spectrum of the mixture of 10 mols. of dinitrogen tetroxide with 90 mols. of sulphuric acid shows all the spectral characteristics of molecular sulphuric acid, except that the weakest frequencies, 976 cm.$^{-1}$ and 1376 cm.$^{-1}$, are not detected, and the two lowest frequencies are not resolved. In addition, three strong frequencies, of about 1045, 1400, and 2300 cm.$^{-1}$, are present. None of these has a counterpart in the Raman spectrum of dinitrogen tetroxide as observed for the solid phase (Sutherland, *Proc. Roy. Soc.*, 1933, *A*, **141**, 342).

A microphotometer record of part of a Raman spectrum of a mixture of dinitrogen tetroxide and sulphuric acid is shown in Fig. 2. The line at 1400 cm.$^{-1}$ has the easily recognisable appearance of the nitronium ion fundamental. The line at 2300 cm.$^{-1}$ can be nothing else than the nitrosonium ion fundamental. The remaining strong frequency, 1045 cm.$^{-1}$, is assigned to the hydrogen sulphate ion. For not only has it the familiar form of the principal Raman frequency of this ion; but also those other spectral appearances which are always associated with the presence of the hydrogen sulphate ion are apparent in this spectrum.

This interpretation of the spectrum requires dinitrogen tetroxide to be ionised by sulphuric acid to produce nitrosonium, nitronium, and hydrogen sulphate ions :

$$N_2O_4 + 3H_2SO_4 = NO^+ + NO_2^+ + 3HSO_4^- + H_3O^+$$

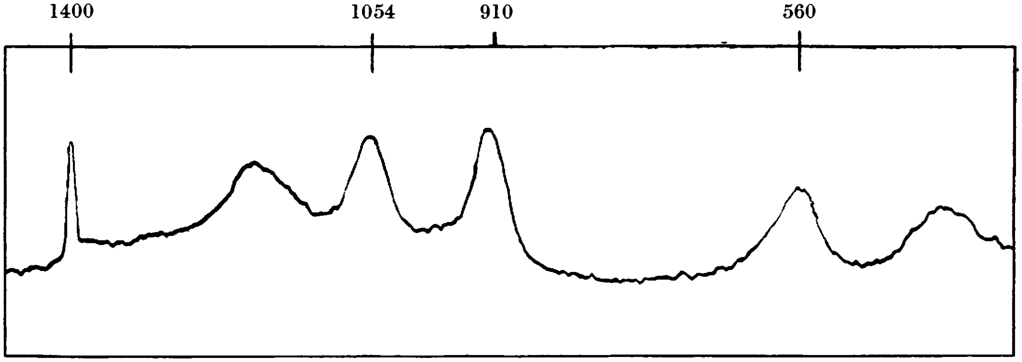
The equation is approximate, inasmuch as it neglects the incomplete ionisation of water by sulphuric acid (Gillespie, *loc. cit.*). It has been roughly confirmed by intensity measurements. Relatively to the hydrogen sulphate ion frequency 1045 cm.$^{-1}$, the nitronium ion line is approximately 1·5 times as intense in the spectra of dilute solutions of nitric acid in sulphuric acid as it is in dilute solutions of dinitrogen tetroxide in sulphuric acid. This agrees with the chemical equations that have been given for the ionisation of nitric acid and of dinitrogen tetroxide in sulphuric acid. Even when allowance is made for the incompleteness of the ionisation of water, the intensity ratio should still be very approximately as stated.

The spectrum of a mixture of 20 mols. of dinitrogen tetroxide with 80 mols. of sulphuric acid generally resembles that of the mixture with only 10 mols. % of dinitrogen tetroxide; but there are differences. The increase in concentration of the tetroxide has resulted in an increase in intensity, relative to the molecular sulphuric acid lines, of the characteristic lines of the hydrogen sulphate ion, the nitrosonium ion, and the nitronium ion. Furthermore, three weak lines are present, which were not found in the spectrum of the more dilute solution of dinitrogen tetroxide. The appearance of these frequencies, 680, 1313, and 1670 cm.$^{-1}$, is attributed to the presence of molecular nitric acid in the mixture. A careful consideration of the known spectra of nitric acid, and its mixtures with sulphuric acid (Part I, *J.*, 1950, 2576), supports the view that the three lines actually have this origin. Evidently the concentrations of nitronium, hydroxonium, and hydrogen sulphate ions have reached such magnitude that a spectroscopically detectable quantity of molecular nitric acid is formed, according to the equation

FIG. 2.

Microphotometer record of part of the Raman spectrum of a mixture of 10 *mols. of dinitrogen tetroxide with* 90 *mols. of sulphuric acid.*

ν *(cm.$^{-1}$) from* Hg 4358 A.



$$NO_2^+ + 2HSO_4^- + H_3O^+ \rightleftharpoons HNO_3 + 2H_2SO_4$$

(3) *Ionisation of Dinitrogen Pentoxide by Sulphuric Acid.*

(3.1) *The Condition of Dinitrogen Pentoxide in Sulphuric Acid.*—Klemenc and Schöller showed (*Z. anorg. Chem.*, 1924, **141**, 231) that solutions of dinitrogen pentoxide in sulphuric acid are very effective nitrating agents, having nitrating properties closely similar to those of solutions of nitric acid in sulphuric acid. They also showed that rate of nitration by a solution of dinitrogen pentoxide is equal to that by a solution of twice as many molecules of nitric acid. These observations are consistent with assumed ionisation of dinitrogen pentoxide and nitric acid by sulphuric acid according to the following equations :

$$N_2O_5 + 3H_2SO_4 = 2NO_2^+ + 3HSO_4^- + H_3O^+$$
$$HNO_3 + 2H_2SO_4 = NO_2^+ + 2HSO_4^- + H_3O^+$$

(3.2) *Raman Spectra of Solutions of Dinitrogen Pentoxide in Sulphuric Acid.*—Table IV contains the results of frequency measurements made on the Raman spectra of sulphuric acid, and of two solutions of dinitrogen pentoxide in sulphuric acid. The recorded frequency displacements (cm.$^{-1}$) were all measured on Stokes lines excited by nitrite-filtered Hg 4358 A.

The spectrum of the more dilute solution of dinitrogen pentoxide in sulphuric acid contains all the characteristic lines of the sulphuric acid molecule, except the two weak ones at 976 cm.$^{-1}$ and 1376 cm.$^{-1}$. It contains in addition two strong lines, one at 1045 cm.$^{-1}$ and the other at 1400 cm.$^{-1}$. The spectrum is, in fact, qualitatively similar to those obtained for solutions of nitric acid in sulphuric acid.

The microphotometric record of the spectrum, reproduced in Fig. 3, shows the now familiar character of the ionic lines at 1400 and 1045 cm.$^{-1}$. There can be no doubt that they belong to the nitronium ion, and the hydrogen sulphate ion, respectively. We also see in the spectrum those other appearances which indicate the presence of the hydrogen sulphate ion, *viz.*, the strong dissymmetry of the line at 560 cm.$^{-1}$, and the oppositely directed and weaker dissymmetry of the line at 910 cm.$^{-1}$.

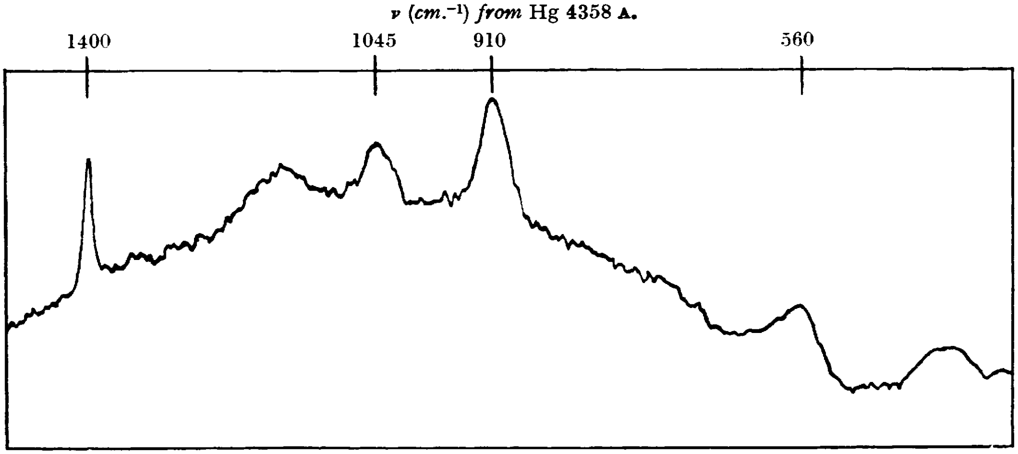
TABLE IV.

Raman frequencies of solutions of dinitrogen pentoxide in sulphuric acid.

Pure H_2SO_4.	N_2O_5 (10 mols.) + H_2SO_4 (90 mols.).	N_2O_5 (30 mols.) + H_2SO_4 (70 mols.).	Pure H_2SO_4.	N_2O_5 (10 mols.) + H_2SO_4 (90 mols.).	N_2O_5 (30 mols.) + H_2SO_4 (70 mols.).
391 (ms)	403 (ms)	407 (ms)	—	1046 (ms)	1044 (s)
416 (ms)			1125—1195 (s)	1160 (s)	1175 (ms)
562 (ms)	565 (ms)	567 (ms)	—	—	1315 (ms)
—	—	610 (w)	1376 (mw)	—	—
—	—	677 (w)	—	1401 (ms)	1402 (s)
912 (s)	910 (s)	907 (s)	—	—	1673 (w)
976 (w)	—	—			

FIG. 3.

Microphotometer record of part of the Raman spectrum of a mixture of 10 *mols. of dinitrogen pentoxide with* 90 *mols. of sulphuric acid.*



These results show that dinitrogen pentoxide is ionised in sulphuric acid according to the approximate equation

$$N_2O_5 + 3H_2SO_4 = 2NO_2^+ + 3HSO_4^- + H_3O^+$$

which disregards the incompleteness of the ionisation of water in sulphuric acid (Gillespie, *loc. cit.*).

Some intensity measurements have been made, which agree with this representation. The ratio of the intensity of the nitronium ion line at 1400 cm.$^{-1}$ to that of the hydrogen sulphate ion line at 1045 cm.$^{-1}$ in spectra of dilute solutions of dinitrogen pentoxide in sulphuric acid, is approximately twice the corresponding ratio for spectra of dilute solutions of dinitrogen tetroxide in sulphuric acid. This is evidently consistent with equations we have written to represent the relevant ionisations.

The spectrum of the mixture of 30 mols. of dinitrogen pentoxide with 70 mols. of sulphuric acid is more complicated than that of the more dilute solution. It contains lines corresponding to all those in the spectrum of the more dilute solution; but the intensities of the lines due to the nitronium and hydrogen sulphate ions are increased relative to the intensities of the molecular sulphuric acid lines. In addition, four lines, which have frequencies of 610, 677, 1315, and 1673 cm.$^{-1}$, are visible. There can be no doubt that these lines are four of the five strongest Raman lines of molecular nitric acid. This is shown by comparisons of both the frequencies and the relative intensities with those observed in the Raman spectra of nitric acid and its mixtures with sulphuric acid (cf. Table II of Part I, *J.*, 1950, 2576). The fifth of the strong, or moderately strong, Raman fundamentals of nitric acid, 925 cm.$^{-1}$, is expected to be visible here only as a deflexion of the contour of the sulphuric acid line at 910 cm.$^{-1}$; such a deflexion is, indeed, observed.

From the evidence it follows that, in the solution containing 30 mols. % of dinitrogen pentoxide, the concentrations of nitronium and hydrogen sulphate ions have reached such values that appreciable quantities of molecular nitric acid are formed by the balanced reaction,

$$NO_2^+ + H_3O^+ + 2HSO_4^- \rightleftharpoons HNO_3 + 2H_2SO_4$$

In other words, the ionic dehydration of dinitrogen pentoxide to the nitronium ion in sulphuric acid can, with an adequate supply of the pentoxide, proceed so far as to produce ionised water in sufficient concentration to rehydrate some of the dinitrogen pentoxide to nitric acid, even in the presence of sulphuric acid.

The author is indebted to Professor C. K. Ingold, F.R.S., for invaluable help and encouragement.

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[*Received, December 17th,* 1949.]