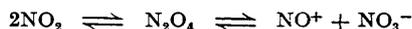


511. Vibrational Spectra of Ionic Forms of Oxides and Oxy-acids of Nitrogen. Part VI. Raman-spectral Evidence of the Ionisation of Dinitrogen Tetroxide in Nitric Acid. The Nitrosonium Ion, NO^+ , and the Nitrosonium-Nitrogen Dioxide Ion, N_2O_3^+ .

By J. D. S. GOULDEN and D. J. MILLEN.

The Raman spectra of solutions of dinitrogen tetroxide in nitric acid have been studied. The spectrum of the dinitrogen tetroxide molecule is completely absent. The strongest appearances, apart from solvent lines, are a line at 2240 cm^{-1} , which can only belong to the nitrosonium ion in some form (see below), and one at 1050 cm^{-1} , which is identified as the main nitrate ion frequency. The latter constitutes an intensification of one of the self-ionisation frequencies of the nitric acid solvent; and, consistently, its development is accompanied by a disappearance of the other self-ionisation line, 1400 cm^{-1} , belonging to the nitronium ion. The solute spectrum contains also a somewhat weak frequency 1380 cm^{-1} , which is assumed to be the totally symmetrical fundamental of the nitrogen dioxide molecule, a frequency hitherto observed only as a weak band in the infra-red. It is concluded that the dinitrogen tetroxide molecule, in dilute solution in nitric acid, is almost completely dissociated, partly homolytically, but chiefly heterolytically, as follows:



The frequency of the nitrosonium ion is usually found at about 2300 cm^{-1} , though the value varies a little with the conditions of solvation. The value 2240 cm^{-1} , obtained in nitric acid, is, however, outside the usual range of variation; and it is shown to arise from a modification of the nitrosonium ion by some specific molecular interaction, because, in the spectra of solutions of nitrosonium hydrogen sulphate and nitrosonium perchlorate in nitric acid, the modified and unmodified frequencies can be seen side by side. By examining the effect of various added substances on the intensities of the modified and unmodified frequencies, the modifying agent is identified as the nitrogen dioxide molecule. It is assumed to form a molecular compound, NO^+NO_2 , held together by a partly homopolar, but mainly electrostatic, one-electron bond.

(1) *Raman Spectra of Solutions of Dinitrogen Tetroxide in Nitric Acid.*

(1.1) *Correlation of Chemical, Electrical, and Spectral Properties of the Solutions.*—It has been suggested (Hughes, Ingold, and Reed, *J.*, 1950, 2400), on the basis of a kinetic study of the effect of dinitrogen tetroxide on nitration in certain media, that the substance is ionised by nitric acid to produce nitrosonium and nitrate ions:



Strong evidence that dinitrogen tetroxide is ionised by nitric acid has been provided by electrochemical work which will be published shortly. It has been shown that solutions of dinitrogen tetroxide in nitric acid have electrical conductances of the same order as those found for solutions of equivalent concentration of alkali nitrates. This establishes not only that dinitrogen tetroxide ionises in nitric acid, but also that it cannot be regarded as a weak electrolyte.

It has also been shown that the addition of alkali nitrates to solutions of dinitrogen tetroxide in nitric acid has the specific effect of increasing the vapour pressure of the solute. The effect may be interpreted as a mass-law repression of the suggested ionisation.

The equation written above for the ionisation of dinitrogen tetroxide in nitric acid has also been used to express the presumed self-ionisation of pure liquid dinitrogen tetroxide (Addison and Thompson, *J.*, 1949, S211 and S218).

The present paper provides Raman-spectroscopic evidence which confirms the suggested ionisation of dinitrogen tetroxide in nitric acid solution. The observation of the Raman spectra of these solutions is rendered difficult by absorption which extends throughout the visible part of the spectrum, is particularly intense in the blue, and continues into the ultra-violet. For this reason we have excited Raman spectra by the green line Hg 5461 Å. In these spectra the strong yellow lines Hg 5770 Å. and Hg 5790 Å. obscure Raman frequencies from about 940 cm^{-1} to 1080 cm^{-1} . By using a technique which reduces the paths of both incident and Raman radiations to a minimum, we have obtained a spectrum of a dilute solution by excitation by Hg 4358 Å., which provides information about that part of the spectrum which is obscured in the spectra excited by Hg 5461 Å.

(1.2) *Raman Spectra of the Solutions compared with the Spectra of the Components.*—The frequencies in the Raman spectra of a number of solutions of dinitrogen tetroxide in nitric acid are recorded in Table I. The frequencies in the spectra of the materials from which the solutions are derived are included for comparison. The Raman displacements which we find for liquid dinitrogen tetroxide at -10° are consistent with those which were found for the solid by Sutherland (*Proc. Roy. Soc.*, 1933, *A*, 141, 342). The Raman spectrum of nitrogen dioxide has not been observed because it absorbs so strongly throughout the visible spectrum. Two of its fundamentals, $\nu_2 = 648 \text{ cm.}^{-1}$ and $\nu_3 = 1621 \text{ cm.}^{-1}$, have been obtained from the infra-red spectrum (Sutherland, *Proc. Roy. Soc.*, 1934, *A*, 145, 278). There are two possibilities for the third fundamental: Sutherland (*loc. cit.*, 1934) and Schaffert (*J. Chem. Physics*, 1933, 1, 507) suppose that the weak band at 1373 cm.^{-1} in the infra-red spectrum corresponds to ν_1 . Harris, Benedict, and King (*Nature*, 1933, 131, 621), in consequence of a study of the ultra-violet absorption spectrum, suggested that ν_1 has the value 1320 cm.^{-1} .†

TABLE I.

Raman frequencies (in cm.^{-1}) of solutions of dinitrogen tetroxide in pure nitric acid.

(The frequencies in cols. 1 and 2 were excited by Hg 4358 Å., and those in cols. 3—7 by Hg 5461 Å. As to col. 8, see the text.)

(1). Pure HNO ₃ .	(2). 1% N ₂ O ₄ in HNO ₃ .	(3). ½% N ₂ O ₄ in HNO ₃ .	(4). 4% N ₂ O ₄ in HNO ₃ .	(5). 6% N ₂ O ₄ in HNO ₃ .	(6). 8.7% N ₂ O ₄ in HNO ₃ .	(7). Liquid N ₂ O ₄ .	(8). Fundamentals of NO ₂ .
609 ms	605 ms	617 ms	602 ms	615 ms	617 ms	265 vs	648
679 ms	675 ms	672 ms	677 ms	690 ms	682 ms	500 m	1320
925 s	925 s	937 s	925 s	925 s	930 s	811 s	or
1049 w*	1045 mw	—	—	—	—	1325 mw	1373
1295 s	1300 s	1305 s	1295 s	1300 s	1307 s	1382 s	1621
1392 w*	—	—	—	—	—	1724 ms	
1533 w	—	1555 w	1532 w	—	1546 w		
1670 m	1680 m	1680 m	1675 m	1685 m	1687 m		
—	—	2232 mw	2238 m	2245 ms	2238 s		

* Self-ionisation line.

The spectrum of the solution excited by Hg 4358 Å. (column 2) shows that, in addition to the frequencies of the nitric acid molecule, there is also present a frequency of 1045 cm.^{-1} . The intense absorption in the blue region shown by the more concentrated solutions has necessitated excitation of Raman spectra by Hg 5461 Å., which carries with it the disadvantage that the frequency 1045 cm.^{-1} will be obscured by the strong yellow lines Hg 5770 Å. and Hg 5790 Å. The spectra given in columns 3—6 contain a frequency of 2240 cm.^{-1} , which increases in intensity with increasing concentration of dinitrogen tetroxide. A frequency of 2240 cm.^{-1} excited by Hg 4358 Å. would fall in a region of the spectrum which is out of focus when the spectrograph is adjusted to record Stokes lines from about 100 cm.^{-1} to 1700 cm.^{-1} , and this is doubtless the reason why this frequency is missing from the spectrum given in column 2.

(1.3) *Spectroscopic Identification of the Ions Present in the Solution.*—The only measured lines of the solutions of dinitrogen tetroxide in nitric acid which cannot be attributed to the nitric acid molecule are those at 1045 cm.^{-1} and 2240 cm.^{-1} . The former appears in the spectrum of anhydrous nitric acid, but there it is accompanied by a line at 1392 cm.^{-1} . It will be recalled that in Part V the frequencies 1045 cm.^{-1} and 1392 cm.^{-1} were assigned respectively to the nitrate and nitronium ions, which are produced, together with a solvated water molecule, by the self-ionisation:



In the spectrum of a dilute solution of dinitrogen tetroxide in nitric acid, the recording of a weak line at 1045 cm.^{-1} in the absence of a line at 1400 cm.^{-1} cannot be due to differential absorption, since this would favour the appearance of 1400 cm.^{-1} . We may easily account for this result if we assume that dinitrogen tetroxide ionises in nitric acid producing nitrate ions. This will lead to a strengthening of the line at 1045 cm.^{-1} , and a reduction in intensity

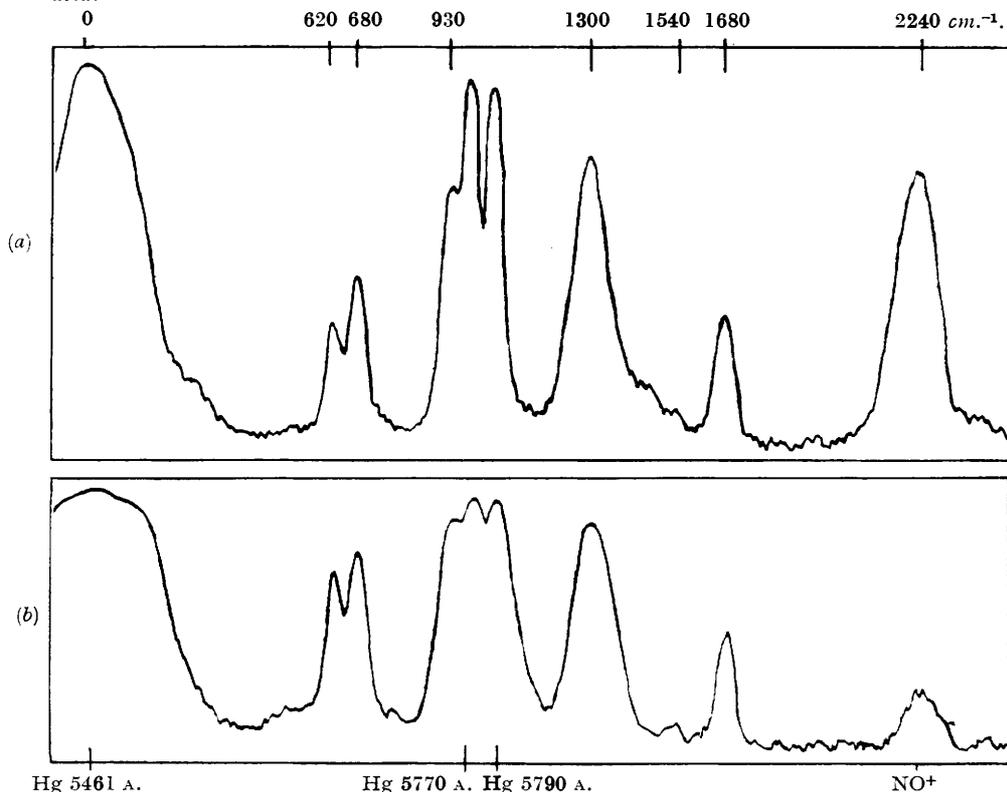
† However, there seems to be an inconsistency somewhere in their analysis, because they find $\nu_2 = 750 \text{ cm.}^{-1}$, whereas it can hardly be doubted that the correct value is the directly observed one, $\nu_2 = 648 \text{ cm.}^{-1}$ (cf. Harris, King, Benedict, and Pearse, *J. Chem. Physics*, 1940, 8, 765).

of the nitronium ion frequency of 1400 cm.^{-1} , as a consequence of the repression of the self-ionisation of nitric acid. The absence of the remaining two fundamental frequencies of the nitrate ion* is attributed to their low intensity compared with the frequency 1050 cm.^{-1} (cf. Part V).

It is seen from columns 7 and 8 of Table I that the frequency 2240 cm.^{-1} is not a fundamental of the nitrogen dioxide or dinitrogen tetroxide molecule. It cannot be an overtone or combination vibration of either of these molecules, for, as the microphotometer record reproduced in Fig. 1 (a) shows, it is too intense to permit this interpretation. We assign the frequency

FIG. 1.

Microphotometer records of the Raman spectra excited by Hg 5461 Å., of (a) a solution, 8.7% by weight, of dinitrogen tetroxide in nitric acid, and (b) a solution, 0.5% by weight, of dinitrogen tetroxide in nitric acid.



to a form of the nitrosonium ion. The highest value of the frequency observed for these solutions is lower than any value hitherto reported for the NO^+ ion, but it is known that the fundamental vibration frequency of the ion is sensitive to change of environment. For crystalline nitrosonium perchlorate the value is 2329 cm.^{-1} (Angus and Leckie, *Trans. Faraday Soc.*, 1935, **31**, 958), while for a solution of dinitrogen trioxide in aqueous sulphuric acid a value for the nitrosonium ion frequency as low as 2290 cm.^{-1} was obtained (Part III, *J.*, 1950, 2600). The significance of the particularly low value of the nitrosonium ion frequency in nitric acid solutions is discussed in Section 2.

The assignments made above lead to the conclusion that dinitrogen tetroxide is ionised in nitric acid according to the equation



There is no spectral evidence of the formation of nitronium or nitrite ions.

* One of them, 720 cm.^{-1} , is doubtfully visible in Fig. 1a. The other, 1360 cm.^{-1} , is overlaid by a stronger frequency of different origin (Section 1.4).

(1.4) *Spectroscopic Evidence concerning the Non-ionised Solute Species.*—The frequencies which appear as separate lines in the spectra of these solutions have now been assigned. It is seen from the microphotometer record of the 8.7% solution (Fig. 1) that in addition to these lines there is an unresolved step-out from the strong nitric acid line at 1300 cm^{-1} . It corresponds to the presence of a frequency of about 1380 cm^{-1} . A nitric acid combination tone and a nitrate ion fundamental occur in this region (Part V, *J.*, 1950, 2612), but the appearance in the present spectrum seems too strong to be attributed to either of these. It may be explained by supposing the solution to contain non-ionised nitrogen dioxide, if the assignment of the fundamentals of this molecule by Sutherland and Schaffert is accepted; for that assignment implies that the strongest Raman frequency of the nitrogen dioxide molecule would have a value of about 1373 cm^{-1} . The yellow colour of the solutions is consistent with the presence of non-ionised nitrogen dioxide. The other two fundamental frequencies of the nitrogen dioxide molecule, 648 cm^{-1} and 1621 cm^{-1} , are not apparent in the microphotometer record reproduced in Fig. 1, but this could hardly be expected since these two frequencies will occur only weakly in the Raman spectrum, and will be masked by the strong nitric acid lines 610 cm^{-1} , 680 cm^{-1} , and 1675 cm^{-1} .

The distinctive characteristics in the spectrum of the dinitrogen tetroxide molecule, which would serve to identify it in the present case, are the strong lines at 810 cm^{-1} and 1722 cm^{-1} , and especially the very strong and sharp line at 265 cm^{-1} . None of these frequencies is evident in the microphotometer records of the spectra of solutions of dinitrogen tetroxide in nitric acid. It may therefore be safely concluded that the concentration of non-ionised dinitrogen tetroxide in these solutions is very small.

(2) *The Influence of Environment on the Nitrosonium Ion Frequency.*

(2.1) *Raman Spectra of Solutions of Nitrosonium Perchlorate and of Nitrosonium Hydrogen Sulphate in Nitric Acid.*—The frequencies in the Raman spectra of 4% solutions of dinitrogen tetroxide, nitrosonium hydrogen sulphate, and nitrosonium perchlorate, and in the spectrum of a 10% solution of nitrosonium hydrogen sulphate are recorded in Table II. The frequencies were measured as Stokes lines excited by Hg 5461 Å. The frequencies recorded in parentheses have been measured as incompletely resolved lines.

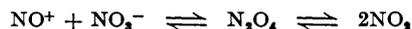
TABLE II.

Raman frequencies (in cm^{-1}) observed in the spectra of nitrosonium salts and dinitrogen tetroxide in nitric acid.

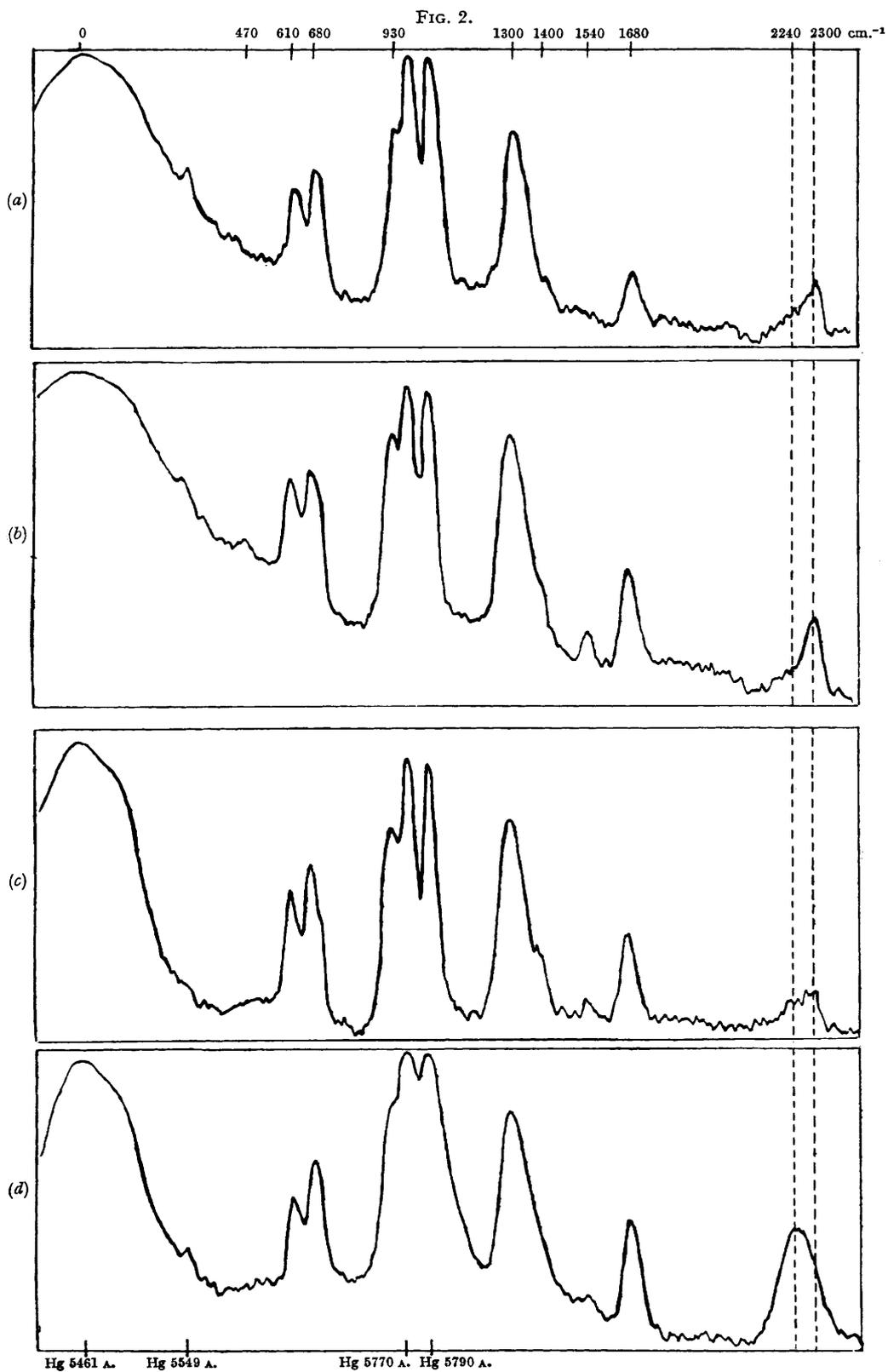
4% N_2O_4 in HNO_3 .	4% $(\text{NO})\text{ClO}_4$ in HNO_3 .	4% $(\text{NO})\text{HSO}_4$ in HNO_3 .	10% $(\text{NO})\text{HSO}_4$ in HNO_3 .	4% N_2O_4 in HNO_3 .	4% $(\text{NO})\text{ClO}_4$ in HNO_3 .	4% $(\text{NO})\text{HSO}_4$ in HNO_3 .	10% $(\text{NO})\text{HSO}_4$ in HNO_3 .
—	471 w	—	—	—	1400 w	1400 w	1400 w
602 ms	617 ms	614 ms	611 ms	—	1533 s	1545 w	—
677 ms	679 ms	677 ms	676 ms	1675 m	1689 m	1680 m	1675 m
925 s	930 s	929 s	928 s	2238 ms	(2240 w)	(2240 mw)	(2243 mw)
1295 s	1302 s	1300 s	1295 s	—	2305 m	(2290 mw)	2285 m

It is seen that, whereas the spectra of solutions of dinitrogen tetroxide contain one line in the region of 2300 cm^{-1} , the spectra of solutions of nitrosonium salts contain two incompletely resolved lines. The weaker component of these has approximately the same frequency as the one line observed in the spectrum of the solution of dinitrogen tetroxide. This is shown clearly in the microphotometer records of the four spectra which are reproduced in Fig. 2.

These results lead to the conclusion that, for solutions in nitric acid, the unmodified nitrosonium ion frequency has a value of about 2300 cm^{-1} , and that under certain conditions the nitrosonium ion may be modified in some manner, which results in a lowering of the frequency to about 2240 cm^{-1} . The molecules which are common to all these solutions, and therefore are possibly the cause of the modification, are the solvent molecule HNO_3 , the molecules H_2O and NO_3^- , derived from the self-ionisation of nitric acid, and the molecules NO_2 and N_2O_4 . The presence of non-ionised nitrogen dioxide in solutions of nitrosonium salts in nitric acid is indicated by the yellow colour of the solution. The nitrogen dioxide is presumably formed in the balanced reaction,



the involved nitrate ion being provided by the self-ionisation of the solvent.



(2.2) *Raman Spectra of Solutions of Dinitrogen Tetroxide in Sulphuric Acid. Effect of the Addition of (a) Water, (b) Nitric Acid.*—The conditions which favour the appearance of the modified nitrosium ion frequency have been investigated by a systematic study of the effect of different added substances.

In order to obtain the number of spectra required, it has been necessary to use arcs producing a higher intensity of 5461 Å. than that obtained from the low-pressure arcs used for the work so far reported. The reduction in exposure time has been accompanied by some loss in resolving power owing to the increased breadth of the line Hg 5461 Å. from the new source.

The results obtained for the addition of water and of nitric acid to a solution of dinitrogen tetroxide in sulphuric acid are given in Tables III and IV, respectively. Only a few of the most characteristic frequencies, which were all measured as Stokes lines excited by Hg 5461 Å., are listed.

TABLE III.

The effect on the Raman spectra of the addition of water to a 10% solution of dinitrogen tetroxide in sulphuric acid.

Mols. H ₂ O Mols. H ₂ SO ₄	Characteristic frequencies (cm. ⁻¹).				Mols. H ₂ O Mols. H ₂ SO ₄	Characteristic frequencies (cm. ⁻¹).			
	NO ₂ ⁺ .	H ₂ SO ₄ .	HNO ₃ .	NO ⁺ .		NO ₂ ⁺ .	H ₂ SO ₄ .	HNO ₃ .	NO ⁺ .
0	1406	905	—	2298	1.07	—	—	—	2288
0.12	1409	906	—	2298	1.51	—	—	1295	2282
0.32	1405	917	—	2299	2.02	—	—	1310	2272
0.53	—	915	—	2288	2.59	—	—	vw	2270
0.67	—	913	—	2289	3.26	—	—	—	2260

TABLE IV.

The effect on the Raman spectra of the addition of nitric acid to a 12% solution of dinitrogen tetroxide in sulphuric acid.

Mols. HNO ₃ Mols. H ₂ SO ₄	Characteristic frequencies (cm. ⁻¹).			Mols. HNO ₃ Mols. H ₂ SO ₄	Characteristic frequencies (cm. ⁻¹).		
	NO ⁺ .	NO ₂ ⁺ .	HNO ₃ .		NO ⁺ .	NO ₂ ⁺ .	HNO ₃ .
0	2299	1410	—	1.0	2292	1410	1310
0.24	2292	1411	—	2.0	2290	1407	1309
0.5	2289	1407	1305				

(2.3) *Raman Spectra of Solutions of Dinitrogen Tetroxide in Nitric Acid. Effect of the Addition of (a) Sulphuric Acid, (b) Water, (c) Dinitrogen Pentoxide.*—The significant frequencies in the spectra of these solutions are recorded in Tables V, VI, and VII. All the frequencies were measured as Stokes lines excited by Hg 5461 Å.

TABLE V.

Effect on the Raman spectra of the addition of sulphuric acid to a 10.6% solution of dinitrogen tetroxide in nitric acid.

Mols. H ₂ SO ₄ /Mols. N ₂ O ₄	0.0	0.019	0.050	0.099	0.497	0.995	1.991	2.982
Mols. HNO ₃ /Mols. H ₂ SO ₄	∞	633	244	124	24.7	12.35	6.18	4.12
Nitrosium ion frequency (cm. ⁻¹)	2243	2248	2246	2250	2260	2290	2297	2296

TABLE VI.

Effect on the Raman spectra of the addition of water to a 11.6% solution of dinitrogen tetroxide in nitric acid.

Mols. H ₂ O/Mols. N ₂ O ₄	0	0.5	1.0	2.0	5.0	10.0	22.1
Mols. H ₂ O/Mols. HNO ₃	0	0.05	0.09	0.18	0.45	0.91	2.00
Nitrosium ion frequency (cm. ⁻¹)	2242	2237	2240	2238	2240	2237	vw

EXPLANATION OF FIG. 2.

Microphotometer records of Raman spectra, excited by Hg 5461 Å., of (a) a solution, 10% by weight, of nitrosium hydrogen sulphate in nitric acid, (b) a solution, 4% by weight, of nitrosium perchlorate in nitric acid, (c) a solution, 4% by weight, of nitrosium hydrogen sulphate in nitric acid, and (d) a solution, 4% by weight, of dinitrogen tetroxide in nitric acid.

TABLE VII.

Effect on the Raman spectra of the addition of dinitrogen pentoxide to a 10% solution of dinitrogen tetroxide in nitric acid.

Mols. N ₂ O ₅ /Mols. N ₂ O ₄	0	0.090	0.183	0.452	0.921	1.424
Mols. HNO ₃ /Mols. N ₂ O ₅	∞	142	69.7	27.8	13.6	8.0
Nitrosonium ion frequency (cm. ⁻¹)	2240	2242	2237	2235	2238	2233

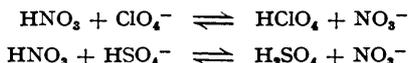
(2.4) *Cause of the Variation of the Nitrosonium Ion Frequency. The Ion N₂O₃⁺.*—For water-sulphuric acid solvents the nitrosonium ion frequency varies continuously from about 2340 cm.⁻¹, for a solution of the hydrogen sulphate in anhydrous acid (Angus and Leckie, *Proc. Roy. Soc.*, 1935, *A*, **149**, 327), to about 2260 cm.⁻¹ for solutions in a largely aqueous medium. The large variation of frequency with change of solvating power of the medium is possibly due to a high polarisability of the triple bond of the nitrosonium ion.

For solutions in nitric acid a different situation arises. Two distinct nitrosonium ion frequencies appear, the lower of which is presumably caused by some specific molecular intervention. It is established by the data in Tables IV, V, VI, and VII that neither nitric acid nor water molecules are concerned in this effect. The presence of nitric acid molecules in the solution does not necessarily result in the appearance of the lower nitrosonium ion frequency, and for solutions in nitric acid neither the addition of water nor its removal by the addition of dinitrogen pentoxide leads to any appreciable change in the nitrosonium ion frequency. The dinitrogen tetroxide molecule may also be excluded since it was shown in Section 1.4 that its concentration in solutions in nitric acid is very small. Evidence that the nitrate ion is not responsible for the modification can also be provided. In an 8.7% solution of dinitrogen tetroxide in nitric acid, nitrosonium and nitrate ions exist in approximately equimolecular proportions, and, as the microphotometer record of the spectrum (Fig. 1) shows, the nitrosonium ion exists in the modified form. But in the spectrum of a 0.31 molal solution of nitrosonium perchlorate, as the microphotometer record of this spectrum (Fig. 2*b*) shows, the unmodified nitrosonium ion frequency appears strongly and the modified one only weakly, although the nitrate ion concentration, provided here by the self-ionisation of the solvent, is about 0.27 molal (cf. Part V). The formation of stable ion-pairs (NO⁺)(NO₃⁻) is also rendered improbable by the high electrical conductance of solutions of dinitrogen tetroxide in nitric acid.

The spectroscopic results are consistent with the idea that the modification of the nitrosonium ion arises through association with nitrogen dioxide. The spectra of solutions of nitrosonium salts in nitric acid are readily interpreted on this basis. The amount of nitrogen dioxide produced in these solutions is controlled by the equilibrium:

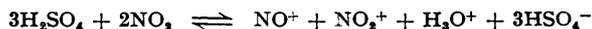


The concentration of nitrate ion depends upon the degree of self-ionisation of nitric acid, and also on the equilibria:



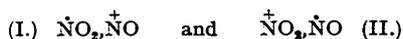
The second of these equilibria will be more important for providing nitrate ions (because sulphuric acid is much less strong than perchloric acid), and therefore the concentration of nitrogen dioxide will be greater in the solution of nitrosonium hydrogen sulphate than in that of the perchlorate. Correspondingly, as the microphotometer records in Fig. 2 show, the intensity of the modified frequency relative to the unmodified frequency is higher in the spectrum of the hydrogen sulphate than in that of the perchlorate.

The frequency of the nitrosonium ion in the spectra of solutions of dinitrogen tetroxide in nitric acid is unaffected by the addition of dinitrogen pentoxide or water (Tables VI and VII). Neither of these substances removes non-ionised nitrogen dioxide, and, consistently, all these spectra contain the modified nitrosonium ion frequency. But the addition of increasing quantities of sulphuric acid, which will remove non-ionised nitrogen dioxide by the reaction



leads to a sharp rise in the nitrosonium frequency, until it reaches the unmodified value for solutions in nitric acid (Table V). Thus the spectral evidence points fairly definitely to the existence of a molecular compound between the ion NO⁺ and the radical NO₂.

It is possible that the compound arises through the formation of a single-electron bond between the ion and the radical, the resonance structures of the compound being



The observed frequency of 2240 cm^{-1} for the compound is much closer to the frequency of the NO^+ ion (2300 cm^{-1}) than to that of the nitric oxide molecule (1880 cm^{-1}). This is taken to indicate the wave-function for structure (I) makes the greater contribution to the real wave-function of the molecule. It is to be expected that structure (I) will be more important than structure (II), since the NO_2 molecule belongs to a lower state of oxidation than the ion NO_2^+ , and the NO^+ ion belongs to a higher state of oxidation than the NO molecule. Thus (I) would have a smaller tendency to pass by a redox electron-transfer into (II) than (II) would have to pass into (I). For these reasons, we regard the ion N_2O_3^+ essentially as a modified nitrosonium ion, and name it, accordingly, the nitrosonium-nitrogen dioxide ion.

(3) Experimental Methods.

The main methods of obtaining and evaluating spectra were similar to those mentioned in Part I, but certain modifications, which were necessitated by the strong colour of the materials, are described here. Spectra were obtained by using an F/4 Hilger E 5 spectrograph, having a mean dispersion of approximately 70 \AA . per mm. for spectra excited by Hg 4358 \AA ., and approximately 150 \AA . per mm. for spectra excited by Hg 5461 \AA . Unless otherwise stated in the text, spectra refer to material at 20°. The experimental arrangements fall into three main classes: excitation by Hg 4358 \AA . using low-pressure arcs; excitation by Hg 5461 \AA . using low-pressure arcs; excitation by Hg 5461 \AA . using medium-pressure arcs.

Solutions of dinitrogen tetroxide in nitric acid absorb so strongly in the blue region that, in order to excite Raman spectra by Hg 4358 \AA ., it was necessary to use a technique in which the paths of both incident and Raman radiations were as short as possible. This was achieved by using a rectangular, fused quartz cell of interior dimensions $2 \times 40 \times 14$ mm. The construction of such a cell, and the method of mounting it on the axis of the collimator of the spectrograph, have been described by Poole (*J.*, 1946, 245). The incident radiation from a vertical, low-pressure, direct-current, mercury arc was focused by an F/1.5 lens on to a point near that end of the cell which was closer to the slit. The Raman radiation which had to traverse only a short path through the liquid was focused by a lens on the slit of the spectrograph. Using Ilford Special Rapid plates, and a slit width of 0.1 mm., a spectrum containing the main nitrate ion frequency was obtained from a 1% solution of dinitrogen tetroxide in nitric acid after an exposure of 170 hours.

The method used for the excitation of Raman spectra by Hg 5461 \AA ., using low-pressure arcs, was similar to that described in Part I for liquids which are available in quantity and are not decomposed by the exciting radiation. The light from the source was approximately focused on the Raman cell by a cylindrical tube 3 cm. in diameter, which was filled with a 40% solution of a mixture of about equal quantities of neodymium and praseodymium chlorides. By using this filter in conjunction with 1 cm. of saturated copper chloride solution in a concentric, annular cell, arranged co-axially with the Raman cell, the spectral background was reduced, weak mercury lines removed, and the intensities of Hg 5770 \AA . and 5790 \AA . were reduced sufficiently to prevent halation on the photographic plate. In fact, under such conditions, these lines were sharp enough to be used as reference lines for measuring purposes.

Raman spectra have also been excited by Hg 5461 \AA ., using 80-watt Osira mercury arcs. The intensity of Hg 5461 \AA . in the radiation from these arcs is much greater than that from the low-pressure arcs, but the line is also broader, and the spectral background in the region 5400–5600 \AA . is much higher. By using these arcs, it was possible to reduce considerably the exposure time required to obtain Raman spectra excited by Hg 5461 \AA ., although this gain was accompanied by some loss in resolving power, and by difficulty in detecting lines at about 600 cm^{-1} . Two "Osira" arcs were placed on each side of the Raman cell, which was 15 cm. long and 2 cm. in diameter. Filters of copper chloride and mixed neodymium and praseodymium chlorides were used as before. With this arrangement it was possible to record, on Kodak P 1200 plates, strong Raman spectra of even a 10% solution of dinitrogen tetroxide in nitric acid with an exposure of 24 hours.

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