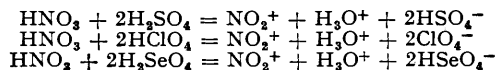


**506. Vibrational Spectra of Ionic Forms of Oxides and Oxy-acids of Nitrogen. Part I. Raman-spectral Evidence of the Ionisation of Nitric Acid by Perchloric, Sulphuric, and Selenic Acids. Spectroscopic Identification of the Nitronium Ion,  $\text{NO}_2^+$ .**

By C. K. INGOLD, D. J. MILLEN, and H. G. POOLE.

This paper extends the account given by Chédin and others of the two Raman lines, 1400 and 1050  $\text{cm}^{-1}$ , which are present, but weak, in the spectrum of nitric acid, are intensified strongly, at the expense of molecular nitric acid frequencies, on the addition of sulphuric acid, or dinitrogen pentoxide, or phosphoric oxide, are repressed again, with restoration of nitric acid frequencies, by the subsequent addition of water, and constitute the sole observed spectrum of solid dinitrogen pentoxide. Hitherto the frequency 1400  $\text{cm}^{-1}$  has always been accompanied by 1050  $\text{cm}^{-1}$ , the two being comparable in intensity over a great range of intensities. The frequency 1400  $\text{cm}^{-1}$  has now been developed without its companion by the addition to nitric acid of either perchloric acid or selenic acid. This shows that the two lines do not come from a common molecular source, and a detailed study of the spectra proves that the source of the frequency 1400  $\text{cm}^{-1}$  has no other line in its spectrum. The source is thus unambiguously identified as the nitronium ion: no other structure, which could be composed from the elements in nitric acid, would yield the observed spectral characters.

The source of the companion frequency 1050  $\text{cm}^{-1}$ , as produced by the use of sulphuric acid, has several other lines in its Raman spectrum: they are shown to belong to, and to identify, the hydrogen sulphate ion. When the frequency 1400  $\text{cm}^{-1}$  is developed by the use of perchloric acid, other Raman lines appear: they belong to, and they identify, the perchlorate ion. When the frequency 1400  $\text{cm}^{-1}$  is developed with the aid of selenic acid, still other lines appear: they belong to, and identify, the hydrogen selenate ion. Generally, every spectral appearance, which could be expected from the following assumed modes of ionisation of nitric acid, is observed:



In the example of ionisation in sulphuric acid, the reversibility of the process is demonstrated, again in extension of Chédin's work. He showed that nitric acid lines, which had been weakened by the addition of sulphuric acid, could be restored by adding water; and it is now shown that they can also be restored by adding potassium hydrogen sulphate. The significance of the other known appearances or intensifications of the frequencies 1400 and 1050  $\text{cm}^{-1}$  is treated in Part V (*J.*, 1950, paper no. 510).

(1) *Objects and Methods.*

(1.1) *Object of this Series of Papers.*—The aim of the work to be described in the papers of this series is the spectroscopic study of the ionic forms assumed by nitric acid, by nitrous acid, and by the related oxides of nitrogen, not only in solution in various types of solvents, but also in the crystalline lattices of salt-like compounds.

The manner in which this problem originally presented itself in connexion with an investigation of the kinetics and mechanism of aromatic nitration is described in an accompanying paper by Hughes, Ingold, and Reed (*J.*, 1950, 2400). The place of the present investigation in the subsequently planned, general study, by the available physical methods, of ionisation phenomena in very strongly acidic solvents such as sulphuric acid, follows fairly obviously from the historical outline of this subject which is given in another of the accompanying papers (Gillespie, Hughes, and Ingold, *J.*, 1950, 2473).

(1.2) *Object of the Present Paper.*—This first paper of the present series deals with the ionisation of nitric acid in three very strongly acidic solvents. The development of this limited section of the wider field of ionisation in such solvents is outlined in yet another of the accompanying papers (Gillespie, Graham, Hughes, Ingold, and Peeling, *J.*, 1950, 2504).

The technique now employed is that of Raman spectroscopy. The three statements to which reference has been made being conveniently available, all we shall have to do, in order to complete the account of the background on which the present work was laid, will be to summarise the results which have been obtained by application of the Raman-spectroscopic technique to our problem. This is done in Section 2.1.

The principal outcome of the work described in this paper has already been reported in summary (*Nature*, 1946, 158, 480).

(1.3) *Experimental Arrangements.*—The main parts of the apparatus, including the spectrograph and the microphotometer, and the general methods of recording and evaluating spectra, were the same

as those which Poole had employed (cf. *J.*, 1946, 245) for the study of the deuterated benzenes, except for modifications necessitated by the different nature of the material now under examination. Such material falls into several classes, each requiring a different experimental arrangement.

One such class consists of liquids which are available in quantity and are not decomposed by the exciting radiation. This class includes sulphuric acid, aqueous sulphuric acid, mixtures of nitric and sulphuric acids containing less than about 80% of nitric acid, and dilute solutions of dinitrogen pentoxide, tetroxide, and trioxide, in sulphuric acid. The cell used for these liquids consisted of a Pyrex tube, 40 cm. long and 2 cm. in diameter, which contained two optical windows 36 cm. apart. These were fixed by shrinking the tube on to them in the blowpipe, and then carefully annealing the whole. The cell was mounted co-axially with the collimator, and a lens was interposed which focused the centre of the more remote window on the slit of the spectrograph. The contents of the cell were illuminated by means of two low-pressure, direct-current, quartz, mercury arcs, about 45 cm. long, each carrying a current of 3.5 amps.

Anhydrous nitric acid and many of its solutions constitute another class of liquid which includes those mixtures of nitric acid with perchloric acid, or sulphuric acid, or selenic acid which contain more than about 80% of nitric acid. Observation of the Raman spectra of these liquids is rendered difficult by decomposition, resulting in a yellow material which absorbs practically all the Raman radiation excited by the mercury lines 4047 Å. and 4358 Å. The decomposition is accelerated by the shorter-wave light from the mercury arc, but is retarded by a reduction of temperature. In order to obtain spectra of satisfactory intensity, it was found desirable to maintain the cell contents below  $-10^{\circ}$ , and to employ Hg 4358 Å. for the excitation, the other violet line, Hg 4047 Å., and the ultra-violet part of the mercury spectrum, being filtered out as completely as possible. The cell was like that described above, except that it was only 10 cm. long and was jacketed. Through the jacket a cooled solution of *m*-dinitrobenzene and rhodamine in alcohol was pumped, which maintained the cell contents at about  $-15^{\circ}$ , and removed the more photochemically active light, thus permitting useful exposures up to about 16 hours. The local heating produced by the arcs was sufficient to keep the outer wall of the cooling jacket free from ice. The cell window nearest to the spectrograph was kept clear by passing a stream of warm, dry air across it.

Liquids available in rather smaller quantity, for instance, solutions of certain sulphates, or disulphates in oleum, were treated by the Wood's-tube method (cf. Poole, *loc. cit.*).

Crystalline solids, such as nitronium salts, were examined as powders, a special system of filters being employed in order to reduce the continuous spectral background and the otherwise excessive amount of light reflected into the spectrograph from the crystal surfaces. The cell consisted of a short Pyrex tube with a window sealed-in near the centre, and a male ground joint at one end. The solid was pressed against the window to form a pellet of depth about 0.5 cm., and the tube was then closed by means of a ground cap, sealed on with metaphosphoric acid. The cell was mounted on the axis of the collimator, and a lens was used in order to focus the Raman radiation on the slit. The light from the lamps passed through concentric, annular, praseodymium and cobalt filters (cf. Poole, *loc. cit.*), arranged co-axially with the cell, and the Raman radiation, on its way to the spectrograph, passed through an *o*-nitrophenol filter, in order to remove some of the surface-reflected light. It was found important to keep the arcs cool by means of an air blast, not only for the purpose of reducing the spectral background, but also in order that they could be placed quite close to the cell, thus increasing the intensity of the irradiation and reducing the needed exposure. The weakest of the perchlorate ion fundamentals, usually described as a diffuse band (cf., however, Part IV), could thus be obtained satisfactorily from powdered perchlorate with an exposure of 70 hours.

(1.4) *Preparation of Materials.*—The methods used for the preparation of most of the materials required for this work are described in accompanying papers (*J.*, 1950, 2400, 2452, 2504, 2559). This applies, in particular, to nitric acid (cf. *J.*, 1950, 2400), but the preparation of the other strong acids requires some description here.

The sulphuric acid used was essentially 100% acid supplied by British Drug Houses Ltd.; but, before use, it was heated at  $100^{\circ}$  for 2–3 hours, in order to secure destruction of a trace of some impurity which caused a troublesome fluorescence under the conditions of excitation of the Raman spectra.

Anhydrous perchloric acid was prepared from 60% acid by distillation from excess of sulphuric acid in an apparatus similar to that used for the preparation of anhydrous nitric acid.

Anhydrous selenic acid was obtained from commercial 92% acid by crystallisation. It was collected by filtration in a stream of dry air, and kept in a vacuum over phosphoric oxide.

Oleum was prepared by redistilling freshly distilled sulphur trioxide under reduced pressure on to solid sulphuric acid at  $-80^{\circ}$ , and allowing the mixture to warm to room temperature. The composition having been controlled by weighing, the oleum was diluted suitably by the addition of 100% sulphuric acid. The diluted oleum was heated at  $100^{\circ}$  for 2–3 hours in order to destroy sources of fluorescence.

## (2) *The Cation in Solutions of Nitric Acid in Very Strong Acids.*

(2.1) *Some Non-mixture-law Lines in the Raman Spectra of Mixtures of Nitric and Sulphuric Acids.*—The intense and very sharp line of frequency  $1400\text{ cm.}^{-1}$ , which the Raman spectra of these mixtures always contain, and which obviously does not belong either to the nitric acid or to the sulphuric acid molecule, was first recorded by Médard (*Compt. rend.*, 1934, 199, 1615). A similar line was found in the Raman spectrum of a solution of dinitrogen pentoxide in nitric acid by Briner and Susz (*Helv. Chim. Acta*, 1935, 18, 378). A weak line of the same frequency was reported by Angus and Leckie in the Raman spectrum of anhydrous nitric acid (*Proc. Roy. Soc.*,

1935, *A*, **149**, 327); but they did not identify it with Médard's line. However, Chédin definitely recognised the weak appearance of Médard's frequency in the spectrum of anhydrous nitric acid; and most of our information about this frequency is due to Chédin (*Compt. rend.*, 1935, **200**, 1397; 1935, **201**, 552, 714; 1936, **202**, 220, 1067; 1936, **203**, 772, 1509; *Ann. Chim.*, 1937, **8**, 243). This Raman line is not only very sharp; it is also highly polarised. Chédin's value for its depolarisation factor is  $\rho = 0.19$ , and an almost identical figure has been recorded by Venkateswaran (*Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 174).

The discovery of Médard's frequency in anhydrous nitric acid showed that the source of the frequency must be some product of a self-reaction of nitric acid. Chédin proved in detail that the frequency is associated with the product of a dehydration of nitric acid. He showed, for instance, that if successive amounts of sulphuric acid are added to nitric acid, the frequency  $1400 \text{ cm.}^{-1}$  will reach a maximum of intensity, while simultaneously the lines of the nitric acid molecule will weaken and finally disappear; and that if, when this has happened, some water is added, it will reduce the intensity of the frequency  $1400 \text{ cm.}^{-1}$ , and at the same time bring back the lines of the nitric acid molecule. Consistently with Briner and Susz's observation, Chédin showed that the frequency  $1400 \text{ cm.}^{-1}$  of anhydrous nitric acid becomes greatly intensified in solutions of dinitrogen pentoxide in nitric acid, or in anhydrous acid to which phosphoric oxide has been added.

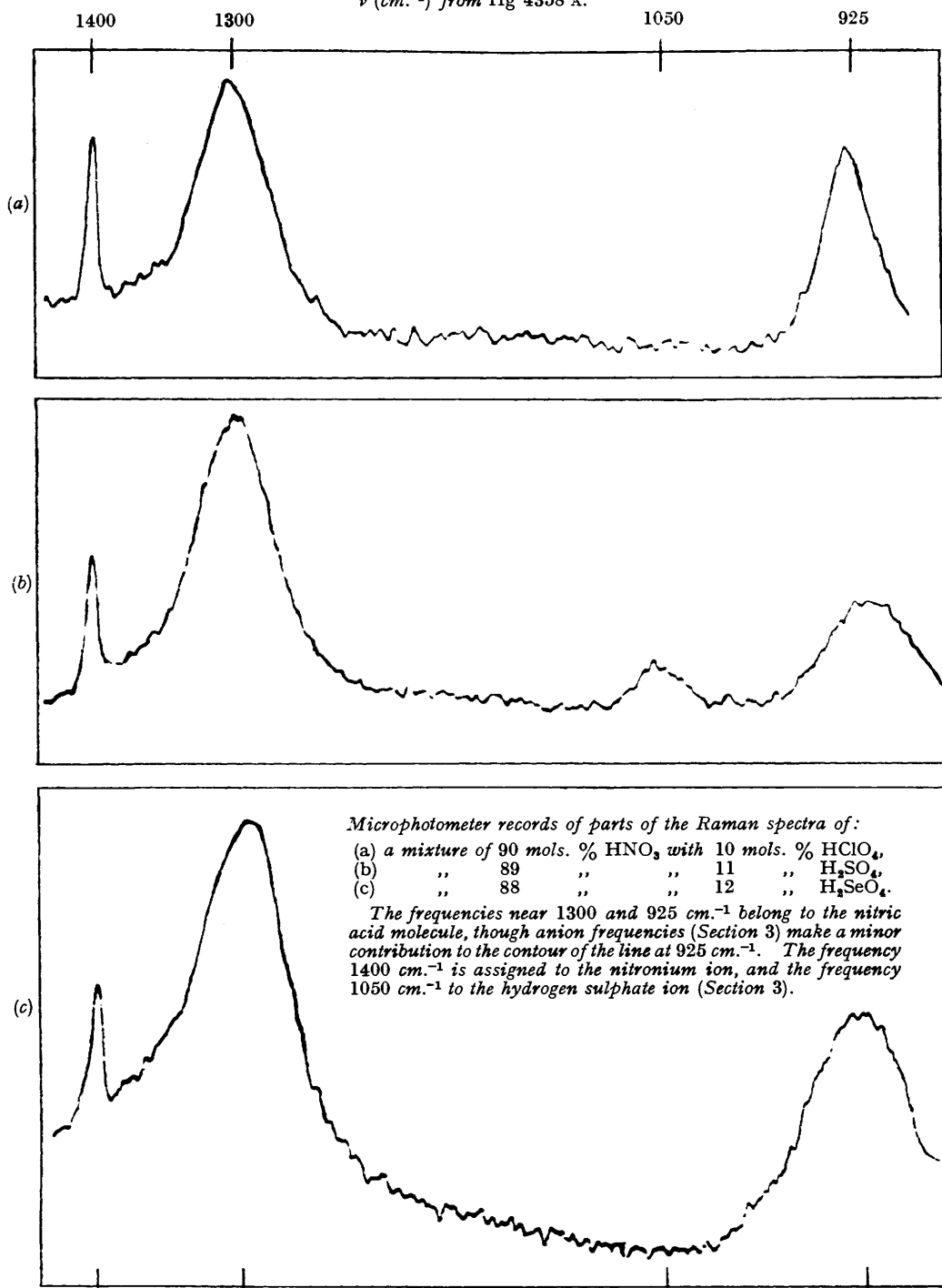
Throughout the above work it was noticed that a second non-mixture-law Raman line, having the frequency of about  $1050 \text{ cm.}^{-1}$ , appeared to be closely associated with the frequency  $1400 \text{ cm.}^{-1}$ . All investigators have found that whenever the frequency  $1400 \text{ cm.}^{-1}$  occurred, the frequency  $1050 \text{ cm.}^{-1}$  occurred also, the two always remaining comparable in intensity over a great range of intensities. Thus, as Angus and Leckie and also Chédin found, both lines occur weakly in the spectrum of anhydrous nitric acid. As Briner and Susz and also Chédin observed, both lines are strongly developed in the spectra of solutions of dinitrogen pentoxide in nitric acid; and likewise, as Chédin found, in the spectrum of nitric acid treated with phosphoric oxide. Chédin showed in detail that, as the composition of mixtures of nitric acid and sulphuric acid was changed, the intensities of the two lines varied in a parallel manner. Finally, Chédin found the same two lines, again together, as the sole visible lines in the Raman spectrum of solid dinitrogen pentoxide.

It was an obvious conclusion from this evidence that the two frequencies,  $1400$  and  $1050 \text{ cm.}^{-1}$ , have a common origin. Briner and Susz originally suggested that they belong to dinitrogen pentoxide. Chédin showed, however, that the Raman spectrum of dinitrogen pentoxide in neutral solvents, and, in particular, in a solvent in which it was known from cryoscopic observations to have a normal molecular weight, is entirely different. He therefore assumed the two frequencies to arise, not from the normal molecule of dinitrogen pentoxide, but from a special form of that substance. Bennett, Brand, and Williams interpreted these results and conclusions on the basis that Chédin's special form is the ionised form (*J.*, 1946, 869). In particular, they assigned the frequency  $1400 \text{ cm.}^{-1}$  to the nitronium ion, comparison with the isoelectronic molecule carbon dioxide having shown that a polarised Raman frequency would be expected in this region. They attributed the frequency  $1050 \text{ cm.}^{-1}$  to the nitrate ion, or, in the presence of sulphuric acid, to the hydrogen sulphate ion, assignments which are consistent with the known spectra of these anions. In the following Sections we shall supply spectroscopic demonstrations of the correctness of these interpretations.

(2.2) *Some Non-mixture-law Lines in the Raman Spectra of Mixtures of Nitric Acid with Perchloric Acid and with Selenic Acid.*—The basis of the method now employed in order to establish the origin of the frequency  $1400 \text{ cm.}^{-1}$  may be explained as follows. Invariably hitherto, the Raman line at  $1400 \text{ cm.}^{-1}$  has appeared in company with the line at about  $1050 \text{ cm.}^{-1}$ , the two having such intensity relations as would indicate a common molecular source. But spectroscopic theory shows that if two such lines should arise from a common source, then that source could not be anything as simple as the nitronium ion, which belongs to the very limited class of molecules that cannot have more than one strong Raman line. We are allowed to assume that the frequency  $1400 \text{ cm.}^{-1}$  belongs to the nitronium ion, if we suppose that the frequency  $1050 \text{ cm.}^{-1}$  arises from some second source, such as an associated anion, which, for stoichiometric reasons, is always formed along with, and in quantity equivalent to, the nitronium ion. However, the simplest way to establish this theory, and, indeed, to prove that the source of the frequency  $1400 \text{ cm.}^{-1}$  has one, and not two, strong lines in its Raman spectrum, would be to isolate the frequency  $1400 \text{ cm.}^{-1}$  from its hitherto constant companion.

The conditions required for doing this are readily predicted. In the first place, the nitrate ion is known to have a strong Raman frequency at about  $1050 \text{ cm.}^{-1}$ , and therefore any nitrate

FIG. 1.  
 $\nu$  ( $\text{cm}^{-1}$ ) from Hg 4358 A.



ion which is, or might be, present in nitric acid, or a mixture containing it, must be excluded. Such nitrate ion could be destroyed by the addition of any acid which is considerably stronger than nitric acid, and would therefore quantitatively transfer a proton to its anion. Sulphuric acid is considerably stronger than nitric acid. But for our purpose the added acid may not be sulphuric acid, because, in transferring its proton to the nitrate ion, this acid would become converted into the hydrogen sulphate ion; and it is known that this ion also has a strong Raman frequency at about 1050  $\text{cm}^{-1}$ . However, the added acid could be either perchloric acid or selenic acid; for these acids are sufficiently strong to destroy the nitrate ion; and neither the perchlorate ion nor the hydrogen selenate ion has a Raman frequency near 1050  $\text{cm}^{-1}$ .

Therefore we have studied the Raman spectra of mixtures of nitric acid with perchloric acid and with selenic acid; and, notwithstanding Chédin's extensive work, we have, for purposes of comparison, made a further examination of the Raman spectra of mixtures of nitric and sulphuric acids.

For each type of mixture several non-mixture-law Raman lines have been observed. It will be shown in Section 3 that all of them but one belong to the anions present in the mixtures. Here we shall confine attention to the occurrence or otherwise of the two non-mixture-law frequencies, 1400 and 1050  $\text{cm}^{-1}$ .

As to this, the results are as follows. In the Raman spectra of mixtures of nitric acid with sulphuric acid, we obtain, as all other investigators have done, the two lines at 1400 and 1050  $\text{cm}^{-1}$ , both strongly developed. But in the Raman spectra of the mixtures of nitric and perchloric acids, and in those of the mixtures of nitric and selenic acids, we find the line at 1400  $\text{cm}^{-1}$  strongly developed, without any trace of an accompanying line at 1050  $\text{cm}^{-1}$ .

This result is established in Fig. 1, which reproduces the microphotometric records of the relevant parts of the Raman spectra of mixtures, approximately corresponding as to molecular composition, of nitric acid with perchloric acid, with sulphuric acid, and with selenic acid. The photographs relating to the mixtures containing perchloric and selenic acid constitute the first records in which the frequency 1400  $\text{cm}^{-1}$  stands isolated from its usual partner.

(2.3) *Spectroscopic Identification of the Nitronium Ion.*—A careful study of such Raman spectra of mixtures as have been illustrated in Section 2.2 has not revealed the presence of any other line which could arise from the same molecular source as that which produces the line at 1400  $\text{cm}^{-1}$ . We have therefore to conclude that the Raman spectrum of this source essentially consists simply of the one strong, highly polarised line having the frequency 1400  $\text{cm}^{-1}$ .

Now there are only two classes of molecules which should have such a Raman spectrum, *viz.*, (1) diatomic molecules, including both the homo- and hetero-nuclear types, AA and AB, and (2) linear, centrosymmetric, triatomic molecules, again including both homo- and hetero-nuclear types, AAA and ABA. Because the spectra of all the chemically stable, diatomic molecules, which can be built from the elements present in nitric acid, are known, all diatomic molecules are excluded from the present assignment. Only two chemically stable, centrosymmetric, triatomic molecules can be constructed from the elements in nitric acid, *viz.*, the azide ion ( $\text{N}=\text{N}=\text{N}$ )<sup>-</sup>, and the nitronium ion ( $\text{O}=\text{N}=\text{O}$ )<sup>+</sup>. We need not here use the chemical argument that the azide ion could not exist in the media in which we find the frequency 1400  $\text{cm}^{-1}$ : its known spectrum suffices to exclude it from the assignment. And thus the nitronium ion is unequivocally identified as the source of the frequency 1400  $\text{cm}^{-1}$  on purely spectroscopic grounds.

The frequency 1400  $\text{cm}^{-1}$  belongs to the totally symmetrical vibration of the nitronium ion. The fundamental frequency of this vibration should appear strongly in the Raman spectrum, and should be represented by a sharp line, having a depolarisation factor of about 0.2, as is observed. This frequency is forbidden in the infra-red spectrum.

The other two fundamental frequencies of the nitronium ion, *viz.*, the non-totally symmetrical non-degenerate (stretching) frequency, and the doubly degenerate (bending) frequency, are forbidden in the Raman effect. But they are allowed in the infra-red, where they have been found,\* as will be reported later.

### (3) *The Anions in Solutions of Nitric Acid in Very Strong Acids.*

(3.1) *Spectroscopic Detection of the Hydrogen Sulphate Ion in Mixtures of Nitric and Sulphuric Acids.*—It is implicit in the foregoing that the frequency 1050  $\text{cm}^{-1}$ , when developed in company with the frequency 1400  $\text{cm}^{-1}$  in the Raman spectra of mixtures of nitric and sulphuric acids, is to be ascribed to the hydrogen sulphate ion. But in order to establish this assignment we must show that all the spectral appearances which are to be expected from the presence of the hydrogen

\* By Mr. H. Cohn, using crystalline nitronium salts.

sulphate ion are to be found in the spectra of the mixtures. This necessitates a somewhat detailed examination of the spectra for the following reasons.

In the first place, sulphuric acid, like nitric acid, gives a fairly rich spectrum of Raman lines; and all the main lines are broad, doubtless on account of the strong intermolecular hydrogen-bonding which occurs in the liquid acid. Then, the majority of hydrogen sulphate ion frequencies must lie quite close to molecular sulphuric acid frequencies. This is to be expected theoretically; for the difference of a proton between the two structures is largely local, affecting mainly one of four similar peripheral masses, and one of four similar radial bonds. Only a few frequencies of the hydrogen sulphate ion, those with much motion of a unique type in the OH-group, can be markedly different from molecular sulphuric acid frequencies. Having regard to the great breadth of the Raman lines of sulphuric acid, it follows that the spectroscopic identification of the hydrogen sulphate ion in the presence of a large excess of sulphuric acid molecules will depend to some extent at least on the detection of heavily overlapped satellite lines, whose presence can be established only by careful study of the microphotometric contours.

According to Woodward and Horner (*Proc. Roy. Soc.*, 1934, *A*, **144**, 129) and others, the hydrogen sulphate ion is characterised by three Raman frequencies which are observably different from molecular sulphuric acid frequencies: in  $\text{cm.}^{-1}$  they are as follows:

590 (m)                      895 (mw)                      1050 (s)

(Here, and later, we use the following contractions as qualitative indications of intensity in Raman spectra: vs = very strong, s = strong, ms = moderately strong, m = medium, mw = moderately weak, w = weak, vw = very weak.)

Of these frequencies, only one occurs in a spectral region almost completely free from molecular sulphuric acid lines. This is the frequency  $1050 \text{ cm.}^{-1}$ , which is much stronger than the others, and is therefore a good index for the hydrogen sulphate ion in sulphuric acid solutions. According to Venkateswaran (*loc. cit.*), this Raman line is considerably polarised. We suppose it to belong to a vibration which essentially involves S-OH stretching, and is rendered markedly different from all molecular sulphuric acid vibrations, and closely similar to what would be a totally symmetrical vibration if the H-atom were on the SO-axis, by accompanying trigonally symmetrical movements of the other three oxygen atoms.

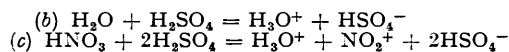
The next of the frequencies of the hydrogen sulphate ion in order of diminishing strength is  $590 \text{ cm.}^{-1}$ ; but this lies so close to the fairly strong molecular sulphuric acid frequency  $560 \text{ cm.}^{-1}$  that it is impossible to resolve them in any known conditions. However, as we shall illustrate below, the presence of the ionic frequency  $590 \text{ cm.}^{-1}$  as a satellite to the stronger molecular frequency  $560 \text{ cm.}^{-1}$  can often be seen rather easily as a dissymmetry in the microphotometric contours of the latter.

The third of the hydrogen sulphate frequencies,  $895 \text{ cm.}^{-1}$ , is not only weaker still, but also it lies still closer to the still stronger and broader frequency,  $910 \text{ cm.}^{-1}$ , of molecular sulphuric acid. In this case the observation of the ionic frequency as a satellite to the molecular frequency is by no means easy; but, as we shall illustrate below, it can just be done, in the conditions which are of interest to us, by means of a careful comparison of line thicknesses.

We record in Table I the results of some measurements of the main Raman frequencies of (a) anhydrous sulphuric acid, (b) a 3M-solution of water in sulphuric acid, and (c) a 3M-solution of nitric acid in sulphuric acid. The listed frequencies are Raman displacements of Stokes lines excited by Hg 4358 Å., simultaneous excitation by Hg 4047 Å. being excluded in the usual manner by means of nitrite filter. The three spectra are reproduced in the form of microphotometer records in Fig. 2.

The most obvious differences between these spectra are that the spectrum of the solution of water contains all the stronger lines of that of the sulphuric acid solvent, together with a line at  $1050 \text{ cm.}^{-1}$ ; whilst the spectrum of the solution of nitric acid contains all the stronger lines of that of the solvent, together with the two lines at  $1050 \text{ cm.}^{-1}$  and  $1400 \text{ cm.}^{-1}$ .

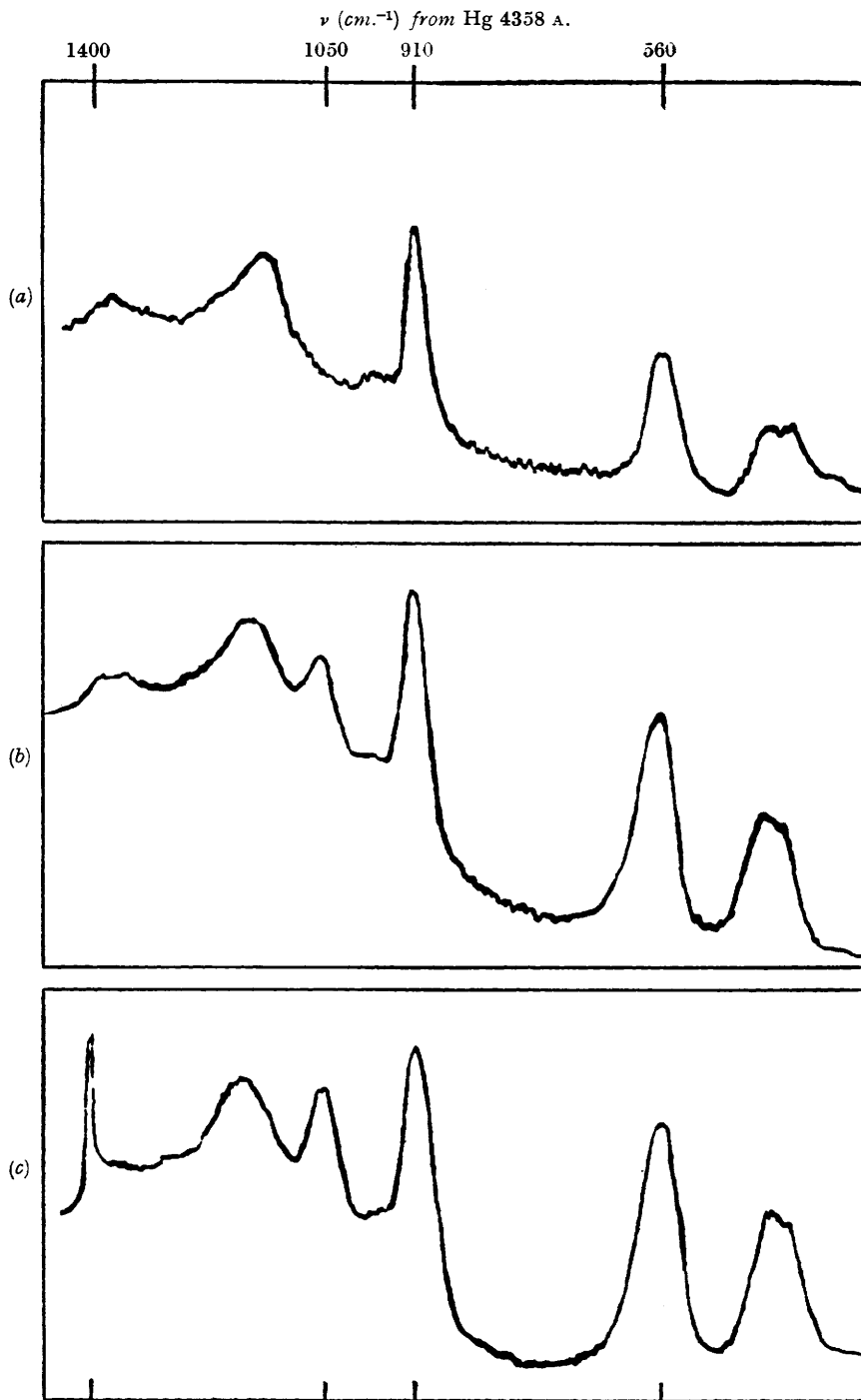
The frequency  $1050 \text{ cm.}^{-1}$  is attributed to the hydrogen sulphate ion formed in solutions (b) and (c) according to the following equations:



Two points of detail, by which this assignment can be supported, are illustrated in the microphotometric records. The first is that the line at  $1050 \text{ cm.}^{-1}$  has the same type of contour in both the spectra in which it occurs. It is a recognisably different contour from that of the identical Raman frequency which can be developed from nitric acid by other means than the addition of

FIG. 2.

*Microphotometer records of parts of Raman spectra of (a) anhydrous sulphuric acid, (b) a 3M-solution of water in sulphuric acid, and (c) a 3M-solution of nitric acid in sulphuric acid.*



sulphuric acid, and which can be shown to be due to the nitrate ion (cf. Part V, Figs. 1 and 2, *J.*, 1950, paper no. 510). The other point is that, relatively to the lines of molecular sulphuric acid, the line at 1050  $\text{cm}^{-1}$  is approximately twice as intense in the spectrum of the solution of nitric acid as it is in that of the equimolar solution of water. This is as it should be, according to the above chemical equations, which, however, neglect the incompleteness in the ionisation of water (Gillespie, *J.*, 1950, 2493); but, even when the incompleteness of ionisation is taken into account, the intensity ratio should still be approximately 2 : 1, as is observed.

TABLE I.

Raman frequencies of (a) sulphuric acid, (b) a 3M-solution of water in sulphuric acid, and (c) a 3M-solution of nitric acid in sulphuric acid.

Solute.	Frequency separation in $\text{cm}^{-1}$ from Hg 4358 A.								
	391	417	562	912	976	—	1125—95	1377	—
(a) None .....	{ ms	{ ms	{ s	{ s	{ w	{ —	{ s	{ mw	{ —
(b) H <sub>2</sub> O .....	{ 393	{ 415	{ 566	{ 914	{ —	{ 1050	{ 1150	{ —	{ —
	{ ms	{ ms	{ s	{ s	{ —	{ ms	{ s	{ —	{ —
(c) HNO <sub>3</sub> .....	{ 392	{ 418	{ 565	{ 911	{ —	{ 1045	{ 1170	{ —	{ 1402
	{ ms	{ ms	{ s	{ s	{ —	{ ms	{ s	{ —	{ ms

It is easy to see that the hydrogen sulphate ion frequency 590  $\text{cm}^{-1}$  is present, not only in the solution of water, but also in that of nitric acid. This is shown by the dissymmetry and basal breadth of the molecular sulphuric acid line at 560  $\text{cm}^{-1}$  in the spectra of the two solutions. These appearances are more marked in the spectrum of the solution of nitric acid than in that of the solution of water, as they should be.

TABLE II.

Raman frequencies of mixtures of nitric and sulphuric acids.

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

Compositions in percentages of nitric acid by volume.

	0.	10.	20.	30.	50.	60.	70.	80.	90.	100.
{	391	392	399	—	—	—	—	—	—	—
{	ms	m	mw	—	—	—	—	—	—	—
{	416	417	415	419	422	421	420	428	428	—
{	ms	ms	m	m	m	m	m	w	vw	—
{	562	564	565	573	573	574	577	580	585	—
{	ms	ms	ms	ms	ms	m	m	m	m	—
{	—	—	—	618	620	621	621	620	615	609
{	—	—	—	m	ms	ms	ms	ms	ms	ms
{	—	—	—	681	681	679	679	679	678	677
{	—	—	—	w	m	ms	ms	ms	ms	ms
{	912	910	908	904	915	932	935	930	927	925
{	s	s	s	s	s	vs	vs	vs	s	s
{	976	—	—	—	—	—	—	—	—	—
{	w	—	—	—	—	—	—	—	—	—
{	—	1045	1043	1043	1044	1045	1049	1050	1053	1049
{	—	ms	s	vs	vs	vs	vs	s	s	w
{	1125—95	1164	1171	1166	1181	1173	1186	—	—	—
{	s	s	ms	ms	m	m	mw	—	—	—
{	—	—	1315	1314	1314	1312	1312	1306	1303	1296
{	—	—	m	ms	s	vs	vs	vs	vs	vs
{	1376	—	—	—	—	—	—	—	—	—
{	w	—	—	—	—	—	—	—	—	—
{	—	1402.1	1401.4	1400.0	1398.3	1398.0	1398.4	1398.7	1396.3	1392
{	—	s	s	vs	vs	vs	s	s	s	w
{	—	—	—	1537	1545	1541	1544	1540	1540	1533
{	—	—	—	vw	w	w	mw	mw	mw	w
{	—	—	—	1666	1680	1675	1674	1675	1676	1670
{	—	—	—	w	mw	m	ms	ms	ms	ms

Even the weak hydrogen sulphate frequency, 895  $\text{cm}^{-1}$ , is discernible in the spectra of the two solutions. It can be seen as a slight, but distinct, thickening of the sulphuric acid line at



910  $\text{cm}^{-1}$ . Consistently, the thickening is appreciably greater in the spectrum of the solution of nitric acid than it is in that of the solution of water.

Some Raman frequencies, which have been measured in the course of a systematic survey of the Raman spectra of a series of mixtures of nitric and sulphuric acids, covering the whole range of composition of such mixtures, are reported in Table II. These results, which are in general agreement with those of Chédin, provide further confirmation of the presence of the hydrogen sulphate ion in the mixtures.

The main general features which these data illustrate are as follows. The spectrum of pure sulphuric acid contains only molecular sulphuric acid lines.\* The spectra of mixtures of the acids made with a sufficiently small proportion of nitric acid, *e.g.*, 10%, contain no molecular nitric acid lines; but they contain molecular sulphuric acid lines, the nitronium ion line at 1400  $\text{cm}^{-1}$ , and the hydrogen sulphate ion line at 1050  $\text{cm}^{-1}$ , as well as the other appearances, indicative of the presence of weak satellite lines, as have already been attributed to the hydrogen sulphate ion. Let us defer for the moment consideration of the mixtures of intermediate compositions. The spectra of mixtures made with a sufficiently large proportion of nitric acid, *e.g.*, 90%, contain no molecular sulphuric acid lines, or at most only one weak one at 428  $\text{cm}^{-1}$ , which might, however, be a weak hydrogen sulphate ion line; instead, these spectra contain molecular nitric acid lines, the nitronium ion line, the strong hydrogen sulphate ion line at 1050  $\text{cm}^{-1}$ , the second hydrogen sulphate ion line at 590  $\text{cm}^{-1}$ , an unresolved low-frequency satellite to the nitric acid line 925  $\text{cm}^{-1}$ , which could be the third hydrogen sulphate frequency 895  $\text{cm}^{-1}$ , and the possible hydrogen sulphate line mentioned above. The spectrum of pure nitric acid contains molecular nitric acid lines, the nitronium ion line, and a line at 1050  $\text{cm}^{-1}$ , which will be shown in Part V to belong to the nitrate ion.

The spectra of all mixtures of intermediate composition contain the strong hydrogen sulphate ion frequency 1050  $\text{cm}^{-1}$ . It is interesting to observe what happens to the weaker hydrogen sulphate ion frequencies as the composition of the mixture changes progressively.

Consider first the frequency 590  $\text{cm}^{-1}$ . As the proportion of nitric acid in the mixed acids is increased from 0% to 90% the frequency at the intensity maximum of the relevant Raman line gradually shifts from 562  $\text{cm}^{-1}$  to 585  $\text{cm}^{-1}$ . The former limit is the molecular sulphuric acid frequency, whilst the latter is essentially the hydrogen sulphate ion frequency. At no intermediate composition are the molecular sulphuric acid line and the hydrogen sulphate ion line resolved from each other: at all such compositions they build up an overlap intensity which is greater than the peak intensity of either component, with the result that the frequency of the observed intensity maximum shifts gradually as the composition of the mixture is progressively altered. That this is the behaviour which should be expected from the interpretation given is clear from recorded observations on the Raman spectra of mixtures of sulphuric acid and water, such as have been investigated by Bell and Jepperson (*J. Chem. Physics*, 1935, 3, 245) and by Woodward and Horner (*loc. cit.*). By increasing the proportion of water in such mixtures from 0% to 90% in stages of 5%, Bell and Jepperson were able to observe only a gradual shift, from 562  $\text{cm}^{-1}$  to 592  $\text{cm}^{-1}$ , of the Raman frequency under consideration, without the least sign of resolution at any intermediate stage.

The third hydrogen sulphate ion frequency, 895  $\text{cm}^{-1}$ , lies so close to the molecular sulphuric acid frequency, 910  $\text{cm}^{-1}$ , that we must expect a similar gradual shift of the relevant Raman line, when the compositions of mixtures containing sulphuric acid are so changed that the content of hydrogen sulphate ion is progressively increased at the expense of the sulphuric acid molecules. Such an effect was, indeed, observed in the work already cited on mixtures of sulphuric acid with water. Thus, on increasing the content of water from 0% to 90%, Bell and Jepperson observed only a gradual fall, from 912  $\text{cm}^{-1}$  to 895  $\text{cm}^{-1}$ , of the Raman frequency. Our result is more complex, *viz.*, that as the content of nitric acid in the mixed acids is increased from 0% to 30% the frequency of the relevant Raman line drops from 912  $\text{cm}^{-1}$  to 904  $\text{cm}^{-1}$ ; but that, on further increasing the proportion of nitric acid, the frequency rises again, its final value in 100% nitric acid being 925  $\text{cm}^{-1}$ . The evident interpretation is that the initial fall of frequency is caused by the partial replacement of sulphuric acid molecules by hydrogen sulphate ions, with partial emergence of the hydrogen sulphate ion line of frequency 895  $\text{cm}^{-1}$  from eclipse by the sulphuric acid line at 910  $\text{cm}^{-1}$ ; and that the subsequent rise in the observed frequency is caused by the incursion, in increasing proportion, of nitric acid molecules, and the consequent resubmergence of the hydrogen sulphate ion line in the strong and broad nitric acid line at 925  $\text{cm}^{-1}$ .

\* Gillespie has shown (*J.*, 1950, 2493, 2516) that pure sulphuric acid contains both hydrogen sulphate and hydrogen disulphate ions, but in quantities too small for detection by present methods.

Reviewing this evidence, we conclude that all those spectral appearances are found which are to be expected on the basis of the theory that mixtures of nitric and sulphuric acid develop hydrogen sulphate ion in approximate accordance with the chemical equation already given.

(3.2) *Spectroscopic Detection of Perchlorate Ion in Mixtures of Nitric and Perchloric Acids.*— In our spectroscopic conditions, it is not possible with mixtures of nitric and perchloric acids, as it is with mixtures of nitric and sulphuric acids, to photograph Raman spectra over the whole range of compositions; because solid substances separate from the mixtures of nitric and perchloric acids, unless a large excess of one of these acids is present. We have given most attention to mixtures containing a large excess of nitric acid, for two reasons. One is that, in these mixtures, perchloric acid molecules are found to have been destroyed so completely that it is a relatively easy matter to prove the presence of perchlorate ions, and, indeed, to show that the whole of the added perchloric acid has been converted into perchlorate ions. The second reason is that, as reported in Section 2.2, we were concerned to establish the absence of an active frequency at  $1050\text{ cm}^{-1}$ ; and, in this demonstration, the presence of any trace of molecular perchloric acid is an embarrassment, because the strongest line in the Raman spectrum of molecular perchloric acid lies at  $1032\text{ cm}^{-1}$ , quite close to the critical part of the spectrum.

A set of frequency measurements, which have been made on the Raman spectrum of a mixture of 10 mols. % of perchloric acid with 90 mols. % of nitric acid, is recorded in Table III. The frequencies are arranged in order to show such relation as they may have to the Raman frequencies of (i) anhydrous nitric acid, (ii) anhydrous perchloric acid, and (iii) the perchlorate ion as observed in aqueous sodium perchlorate. The data for perchloric acid and the perchlorate ion are due to Redlich, Holt, and Bigeleisen (*J. Amer. Chem. Soc.*, 1944, 66, 13).

TABLE III.

*Raman frequencies of a mixture of nitric and perchloric acids. Comparison with the Raman frequencies of anhydrous nitric acid, anhydrous perchloric acid, and aqueous sodium perchlorate.*

(Frequency separations in $\text{cm}^{-1}$ from Hg 4358 A.)			
Anhydrous $\text{HNO}_3$ .	$\text{HClO}_4$ (10 mol. %); $\text{HNO}_3$ (90 mol. %).	Aqueous $\text{NaClO}_4$ .	Anhydrous $\text{HClO}_4$ .
—	—	—	425 (w)
—	463 (mw)	464 (m)	—
—	—	—	572 (m)
—	—	—	585 (mw)
609 (ms)	616 (m)	631 (ms)	—
677 (ms)	678 (ms)	—	—
—	—	—	738 (m)
925 (s)	938 (s)	940 (vs)	—
—	—	—	1032 (s)
1049 (w)	—	1053—1167 (w, band)	—
—	—	—	1182—1312 (w, band)
1296 (vs)	1307 (vs)	—	—
1392 (w)	1397 (s)	—	—
1533 (w)	—	—	—
1670 (ms)	1679 (m)	—	—

It is evident from these figures that none of the molecular perchloric acid lines, not even the strongest at  $1032\text{ cm}^{-1}$ , appears in the spectrum of the mixture. It is also plain that all the molecular nitric acid lines, except the weakest at  $1533\text{ cm}^{-1}$ , are measured in the spectrum of the mixture. One weak line in the spectrum of anhydrous nitric acid, that near  $1400\text{ cm}^{-1}$ , is greatly intensified in the spectrum of the mixture: this is the nitronium ion line (cf. Section 2.3). Another weak line in the spectrum of anhydrous nitric acid, that near  $1050\text{ cm}^{-1}$ , is absent (cf. Fig. 1a) from the spectrum of the mixture: this is the nitrate ion line (cf. Part V). Having dealt with these frequencies, we shall now show that all those appearances in the spectrum of the acid mixture which still remain for consideration are to be attributed to the perchlorate ion.

This tetrahedral ion possesses four fundamental frequencies all active in the Raman effect. By far the strongest is the totally symmetrical frequency,  $940\text{ cm}^{-1}$ . It is not only strong, but also sharp. In the Raman spectrum of the mixture, this strong and sharp perchlorate ion line at  $940\text{ cm}^{-1}$  overlaps the strong and broad nitric acid line at  $925\text{ cm}^{-1}$ . Although

molecular nitric acid is in large excess over perchlorate ion, the combined line derives its peak frequency, 938  $\text{cm}^{-1}$ , essentially from the perchlorate ion component, because of the sharpness of this frequency. Of course, the combined line derives its breadth essentially from the nitric acid component.

The next perchlorate ion frequency in order of strength is 631  $\text{cm}^{-1}$ , which belongs to one of the degenerate bending vibrations. This Raman line is rather broad, as also is the neighbouring nitric acid line at 609  $\text{cm}^{-1}$ . In the spectrum of the acid mixture, these two lines coalesce, giving, as might be expected, an overlap intensity having its maximum at a frequency, 616  $\text{cm}^{-1}$ , lying between the frequencies of the separate components.

The third frequency of the perchlorate ion, 464  $\text{cm}^{-1}$ , belongs to the other degenerate bending vibration. It is not very strong in the Raman effect, but it happens to lie in a region in which it can be observed without disturbance from nitric acid lines. Consistently we find this frequency in the spectrum of the acid mixture, in exactly the right position, and with the expected breadth and intensity.

The fourth fundamental frequency of the perchlorate ion belongs to the triply degenerate stretching vibration. It is represented in the Raman spectrum by the faint, diffuse band \* at 1053—1167  $\text{cm}^{-1}$ . This band cannot be photographed except with the aid of long exposures. As was explained in Section 1.3, long exposures are inapplicable to all mixtures containing nitric acid in proportions greater than about 80%, because yellow material is developed, which absorbs the Raman radiation. Thus the weak band of the perchlorate ion spectrum is not observed in the spectrum of the mixture; but it is not an appearance which we can expect to observe. Summarising, we may say that, without exception, all those appearances are observed in the spectrum of the mixed acids which the presence of the perchlorate ion is expected to produce.

TABLE IV.

*Raman frequencies of a mixture of nitric and selenic acids. Comparison with the Raman frequencies of anhydrous nitric acid, anhydrous selenic acid, and aqueous selenic acid.*

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

Anhydrous $\text{HNO}_3$ .	$\text{H}_2\text{SeO}_4$ (12 mol. %); $\text{HNO}_3$ (88 mol. %).	$\text{H}_2\text{SeO}_4$ (92.5%); $\text{H}_2\text{O}$ (7.5%).	Anhydrous $\text{H}_2\text{SeO}_4$ .
—	296 (mw)	299 (ms)	294 (m)
—	350 (mw)	374 (ms)	{ 361 (ms)
			{ 388 (ms)
609 (ms)	618 (ms)	—	—
677 (ms)	678 (ms)	—	—
—	742 (ms)	747 (s)	756 (vs)
—	867 (ms)	862 (ms)	—
—	—	—	914 (s)
925 (s)	933 (s)	927 (mw)	—
—	—	951 (w)	—
—	—	—	996 (m)
1049 (w)	—	—	—
1296 (vs)	1306 (vs)	—	—
1392 (w)	1398.4 (s)	—	—
1533 (w)	1540 (w)	—	—
1670 (m)	1680 (m)	—	—

(3.3) *Spectroscopic Detection of Hydrogen Selenate Ion in Mixtures of Nitric and Selenic Acids.*—It is not conveniently possible in our conditions to record Raman spectra of mixtures of nitric and selenic acids over the total range of compositions, because selenic acid is a solid at ordinary temperatures. Again we have studied principally mixtures containing a large excess of nitric acid. A set of frequencies is given in Table IV, which have been measured in the Raman spectrum of a mixture of 12 mols. % of anhydrous selenic acid with 88 mols. % of anhydrous nitric acid. The set of frequencies is arranged in the Table in order to show such relation as they have to the known Raman frequencies of nitric acid and of selenic acid, as well as to the frequencies of the hydrogen selenate ion, as far as these are known from observations on the Raman spectra of aqueous selenic acid. The Raman frequencies which are quoted in the Table for anhydrous selenic acid and for an aqueous selenic acid containing 7.5% by weight of water are due to Venkateswaran (*Proc. Indian Acad. Sci.*, 1936, A, 3, 3070).

\* The reason why this fundamental vibration is represented by a band, and not by a line, is explained in Part IV (*J.*, 1950, paper no. 509).

The most obvious feature of the spectrum of the acid mixture is that it contains all the lines of molecular nitric acid. The nitronium ion frequency and the nitrate ion frequency, which appear weakly in the spectrum of molecular nitric acid, behave in the spectrum of the acid mixture, exactly as they do in that of the mixture with perchloric acid: the former frequency becomes greatly intensified, whilst the latter disappears. Apart from all these frequencies, the spectrum of the acid mixture contains four others, *viz.*, 296, 350, 742, and 867  $\text{cm.}^{-1}$ , which are obviously connected with either the hydrogen selenate ion or the selenic acid molecule, and therefore require further discussion.

Similarly to sulphuric acid and the hydrogen sulphate ion, selenic acid and the hydrogen selenate ion possess a number of Raman frequencies which are nearly identical, each with each, whilst some Raman frequencies of the molecule, and some of its anion, are distinct, and therefore are of diagnostic value. Let us consider first these characteristic frequencies. The selenic acid molecule has two, *viz.*, those represented by the strong Raman line at 914  $\text{cm.}^{-1}$ , and by the line of moderate intensity at 996  $\text{cm.}^{-1}$ . Neither can be seen in the Raman spectrum of the mixed acids. The former might be difficult to observe in the presence of the nitric acid line at 925  $\text{cm.}^{-1}$ , but the latter should be easily visible if molecular selenic acid were present. Therefore it is clear that molecular selenic acid is absent.

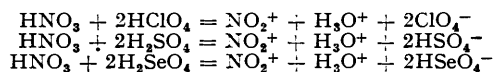
The hydrogen selenate ion has a highly characteristic frequency 862  $\text{cm.}^{-1}$ . It is almost certainly a "breathing" frequency, corresponding to the frequency 1050  $\text{cm.}^{-1}$  of the hydrogen sulphate ion. It is well separated from any line of the selenic acid molecule, and from any line in the nitric acid spectrum. We find it well developed in the spectrum of the acid mixture. It is therefore certain that this mixture contains hydrogen selenate ion. Indeed, it is evident, taking account of the absence of the selenic acid frequencies, that practically the whole of the originally added selenic acid must have been converted into hydrogen selenate ion. The hydrogen selenate ion also has a characteristic, but rather weak, line at 927  $\text{cm.}^{-1}$ , with a still weaker satellite at 951  $\text{cm.}^{-1}$ ; but these lines are of no diagnostic value in the present case, owing to the strong and broad nitric acid line at 925  $\text{cm.}^{-1}$ , which obscures them.

The other three frequencies which we observe in the spectrum of the acid mixture, *viz.*, 296, 350, and 742  $\text{cm.}^{-1}$ , are all frequencies which are approximately identical in the hydrogen selenate ion and the selenic acid molecule. As to the first two, this conclusion was drawn by Venkateswaran himself; but it is equally applicable to the third, as his records of observed intensities show. In the spectrum of the acid mixture, these three frequencies must come from the hydrogen selenate ion.

The four Raman frequencies, 296, 350, 742, and 867  $\text{cm.}^{-1}$ , comprise all the known frequencies in the hydrogen selenate ion spectrum, apart from such as would be obscured by the Raman lines of nitric acid. Thus, not only does no feature of the spectrum of the acid mixture remain unexplained, but also all appearances which are to be expected from the presence of the hydrogen selenate ion are observed.

#### (4) *Reversibility of the Ionisation of Nitric Acid in Very Strong Acids.*

The effect of the spectral analyses described in Sections (2) and (3) has been to establish the formation of all the ions shown on the right-hand sides of the following equations, excepting the hydroxonium ion, which, as is well known, cannot be detected in Raman spectra:



It has been shown also that, in the presence of an excess of nitric acid, the whole of the second acid is destroyed; whilst, in the presence of excess of sulphuric acid, the whole of the nitric acid is destroyed.

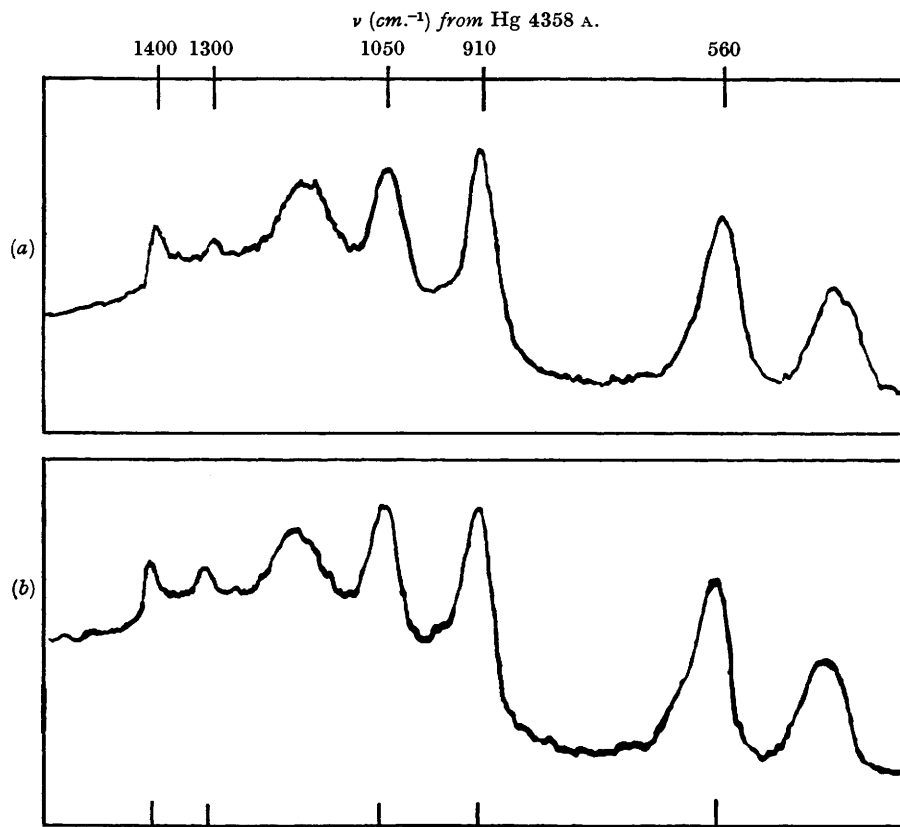
We describe in this Section an experiment which definitely establishes, in the example of the reaction between nitric and sulphuric acids, the reversibility of the closely analogous reactions written above. The method employed is essentially the same as that by which Chédin proved the dehydrating character of the action of sulphuric acid on nitric acid, by following the restoration of molecular nitric acid on adding water. In our experiment, a mixture of nitric and sulphuric acids was prepared, with the constituents in such proportions that almost all the molecular nitric acid was converted into nitronium ion. This solution was then divided into two parts, to one of which potassium hydrogen sulphate was added. Then the Raman spectra of the untreated and hydrogen-sulphate-treated mixtures were recorded under identical optical

conditions. A comparison of the spectra showed that the added potassium hydrogen sulphate had produced a partial regeneration of nitric acid molecules.

This experiment is illustrated by the microphotometric records shown in Fig. 3. Record (a) relates to a solution of 12.5% by weight of nitric acid in 87.5% of sulphuric acid. Record (b) relates to a part of the same solution which has been saturated with potassium hydrogen sulphate before the exposure.

FIG. 3.

*Microphotometer records of parts of the Raman spectra, excited by Hg 4358 Å. filtered through nitrite, of (a) a solution, 12.5% by weight, of nitric acid in sulphuric acid, and (b) the same solution after being saturated with potassium hydrogen sulphate. (Most of the contour of the line at 1400  $\text{cm}^{-1}$  is absent, because the extreme sharpness of this line causes the recording light ray of the microphotometer to travel over the recording paper too rapidly to leave a clearly visible trace.)*



Spectrum (a) contains all the stronger Raman lines of molecular sulphuric acid. It also contains, very strongly developed, the nitronium ion frequency, 1400  $\text{cm}^{-1}$ , and the strong and characteristic hydrogen sulphate ion frequency, 1050  $\text{cm}^{-1}$ . It shows the marked dissymmetry and broadening of the sulphuric acid line at 560  $\text{cm}^{-1}$ , and the similar but weaker appearance associated with the sulphuric acid line at 910  $\text{cm}^{-1}$ , effects which, as we saw in Section 3.1, arise from the presence of the hydrogen sulphate ion. It shows one further line, appearing with rather less than moderate intensity, *viz.*, the line at 1300  $\text{cm}^{-1}$ . This is the strongest line in the Raman spectrum of nitric acid, and, in record (a), it constitutes all that can be seen of the spectrum of molecular nitric acid.

Spectrum (b) contains all the stronger lines of molecular sulphuric acid, and the strongly developed nitronium ion line, as well as the characteristic hydrogen sulphate ion frequency, and those contour-deformations of sulphuric acid lines which are caused by the hydrogen sulphate ion. It is to be noted that all the spectral effects directly due to the hydrogen sulphate ion are stronger than before. Thus, the contour of the hydrogen sulphate ion line at 1050  $\text{cm}^{-1}$  now stands up higher relatively to other lines; and the sulphuric acid lines at 560  $\text{cm}^{-1}$  and 910  $\text{cm}^{-1}$

are each appreciably thicker and more dissymmetric than before. The most interesting relative difference of intensity, however, relates to the remaining line in the spectrum, *viz.*, the molecular nitric acid line at  $1300\text{ cm.}^{-1}$ . This is approximately twice as intense in record (b) as in record (a), clearly showing that molecular nitric acid has been regenerated by the added potassium hydrogen sulphate.

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