POLARISATION OF RAMAN LINES IN SOME INORGANIC ACIDS.

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1. *Introduction.*

A considerable volume of experimental data has been obtained in recent years from the study of the Raman spectra regarding the progressive dissociation of strong electrolytes in concentrated aqueous solutions. It has been found that changes from the covalent to the electrovalent form take place in them in a manner not contemplated by the Debye-Hückel theory of complete ionisation, the point of transition depending on the strength of the acid and the state in which it exists. Thus the halogen hydrides give rise to Raman lines when they are in the state of solid, liquid or vapour or in solution in non-polar solvents[1] indicating that they are covalent in such cases; but even in concentrated solutions in water or other polar solvents they change to the electrovalent form and consequently do not yield any line. On the other hand, the monobasic acids like nitric[2] or iodic[3] acids yield a large number of Raman lines the relative intensities of which change according to the degree of concentration of the acid in water and are interpreted on the assumption that in the more concentrated solutions the percentage of undissociated molecules is great and goes on diminishing with dilution. The polybasic acids, namely, sulphuric,[4] selenic,[5] selenious[6] and phosphoric acids,[7] likewise reveal that the dissociation is not only progressive but stepwise in character and is a function of concentration.

Though the changes in the relative shifts and intensities of the Raman lines at various dilutions of these acids have been qualitatively interpreted as due to progressive ionisation, no attempt has hitherto been made to assign

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[1] West, Wm., and Arthur, P., *Jour. Chem. Phys.*, 1932, **2**, 215.

[2] Rao, I. R., *Proc. Roy. Soc.*, A, 1930, **127**, 279.

[3] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 119.

[4] Nisi, H., *J. J. Phys.*, 1929, **5**, 119.

[5] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 307.

[6] Venkateswaran, C. S., *Ibid.*, 1936, **3**, 533.

[7] Venkateswaran, C. S., *Ibid.*, 1936, **3**, 25.

the lines to any particular mode of oscillation of the molecular species concerned. For this purpose it appears necessary to have a knowledge of the state of polarisation of the lines themselves. A proper identification of frequencies corresponding to similar modes of oscillation in the different units arising from the ionisation of the molecules could also be expected to give us a better knowledge of the mechanism of the changes that take place in the molecule undergoing dissociation. The present paper concerns itself with the state of polarisation of the Raman lines of nitric, iodic, sulphuric, selenic and selenious acids and its significance in relation to the molecular structure of these acids.

2. *Experimental Arrangements and Results.*

The acids used in the investigation were all taken from freshly opened bottles of the purest stock of Kahlbaum chemicals and were fairly free from dust. The iodic and the selenious acids were crystallised out of carefully filtered aqueous solutions and redissolved in double-distilled water. A few drops of nitric acid were added to concentrated sulphuric acid in order to render the latter free from fluorescence.[8] A Hewittic quartz mercury burner served as the source of illumination and was focussed by means of a large glass condenser on the Raman tube which was held horizontally along the axis of the spectrograph. The horizontal and the vertical components of the scattered radiation were separated by interposing a suitably oriented large quartz double-image prism between the slit of the spectrograph and the observation end of the tube. The two components were focussed one above the other on the slit and recorded simultaneously and for the same time on the photographic plate. Specially backed Ilford golden isozenith plates were used and the developing solution and the time of development were kept identical throughout. The ratio of intensities of the horizontal and the vertical components of each of the Raman lines was determined with the help of a Moll microphotometer. Since a high degree of accuracy in the depolarisation measurements is not attempted the intensities of lines excited by 4358 radiations of the source in the various plates were read off from the same density log intensity curve of the microphotometer for the 4600 region of the spectrum. In view of the fact that only the ratio of the intensities of the two components appearing at constant wave-length is desired, the error introduced by the variable sensitiveness of the photographic plate is not considerable. As has been pointed out by previous investigators,[9] the state of polarisation determined in this manner would involve errors due to

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[8] Médard, L., *Compt. Rend.*, 1934, **199**, 1615.

[9] Bhagavantam, S., *Ind. Jour. Phys.*, 1930, **5**, 59.

lack of strict transversality between the directions of incidence and observation and also due to oblique refraction at the surface of the prisms. These errors were determined as follows:—The polarisation characters of the principal Raman lines of CCl_4 were ascertained under identical circumstances and assuming the known values of polarisation of these lines the required error was evaluated. The results given in the present paper give the upper limit of the depolarisation ratios of the lines and are probably correct to ± 5%.

The results are given in Tables I—V. The frequency ν in cm.$^{-1}$ of the line is given in the first column, the intensity I of the line in the second and the corrected depolarisation ratio ρ in the third. In the case of extremely weak lines, the state of depolarisation is indicated by D and P where D

TABLE I (*a*).

Nitric Acid 70%.

No.	1	2	3	4	5	6	7	8	9	10
ν in cm.$^{-1}$ ..	638	697	924	1050	1126	1297	1389	1537	1611	1699(?) 3466
I	4	6	6 br	10	1	8 br	2 br	1	2	3
ρ	0·71	0·62	0·17	0·17	0·70	0·30	0·63	$\approx$0·8	0·5	0·3
ρ (Previous) ..	0·30	0·20	0·20	0·10	..	0·10	..	..	..	..

TABLE I (*b*).

Nitric Acid 25%.

No.	1	2	3	4	5	6
ν in cm.$^{-1}$ ..	726	924	1048	1297	1389	Water band
I	3	0	10	2	3 br	Strong
ρ	$\approx$0·82	P	0·16	P	$\approx$0·85	0·55

TABLE II.

Iodic Acid 6 N.

No.	1	2	3	4	5	6
ν in cm.$^{-1}$ ..	330	463	644	789	823	Water band
I	8	1	6	10	6	Medium strong
ρ	0·60	P	0·30	0·25	0·25	0·60

TABLE III (*a*).

Sulphuric Acid 99%.

No.	1	2	3	4	5	6	7	8
ν in cm.$^{-1}$ ..	384 to 434	564	916	970	1045	1140	1364	1398 (N_2O_5)
I	4 br	6	10	0	4	4 br	0	2
ρ	0·7—0·75	$\approx$0·81	0·16	D	0·32	0·62	D	0·20

TABLE III (*b*).

Sulphuric Acid 25%.

No.	1	2	3	4	5	6	7	8	9
ν in cm.$^{-1}$ ..	427	593	896	982	1047	1172	1223	1334	Water band
I	3	4	2	6	6	1	1	2	Strong
ρ	>0·75	>0·76	0·17	0·03	0·24	D	D	0·77	0·56

TABLE IV.

Selenic Acid (molten).

No.	1	2	3	4	5	6	7
ν in cm.$^{-1}$ ..	294	361	388	756	914	996	1105 1186
I	3	6	6	10	8	3	0
ρ	D	>0·76	>0·77	0·30	0·30	0·70	0·5

TABLE V.

Selenious Acid (molten).

No.	1	2	3	4	5	6	7
ν in cm.$^{-1}$ ..	238	343	380	545	690	862	910
I	1	4	3	1	10	10	3
ρ	D	>0·79	≈0·81	P	0·5	0·5	0·44

means that the depolarisation ratio is nearly equal to 6/7 and P means that it is less than 6/7.

3. *Discussion of Results.*

Nitric Acid.—The Raman spectrum of this acid has been investigated thoroughly from the point of view of electrolytic dissociation by numerous investigators notably by Rao[10] and recently by Médard.[11] Dadieu and Kohlrausch[12] have examined the acid with special reference to its constitutional form. In general, the concentrated solution of this acid yields ten Raman lines with the following mean frequency shifts :—638 (4), 697 (6), 924 (6 br.), 1050 (10), 1126 (1), 1297 (8 br.), 1389 (2 br.), 1537 (1), 1611 (2) and 1699 (4). At a concentration of about 25% all except three lines at 726, 1048 and 1389 practically disappear and hence are attributed to the undissociated molecule. The latter three lines which are also present in the solutions of nitrates are assigned to the nitrate ion. Very intense photographs of the Raman spectra of this acid obtained by the author and reproduced in the accompanying plate confirm the above results of the previous investigators.

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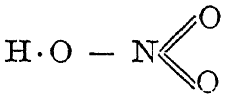
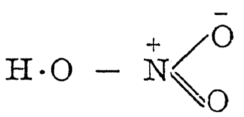
[10] Rao, I. R., *Loc. cit.*

[11] Médard, L., *Compt. Rend.*, 1934, **198**, 1407.

[12] Dadieu and Kohlrausch, *Naturwissenschaften*, 1931, **19**, 690.

The state of polarisation of these lines of the acid at the two specified concentrations is given in Table I. The results of a previous investigation of the polarisation of some of the lines of the 70% acid by Venkateswaran[13] are given in the fourth column and reveal large differences which cannot be explained mainly by the errors of measurement. As is to be expected from the plane symmetrical structure of the NO_3' ion the single and parallel vibration with a frequency shift of 1048 $cm.^{-1}$ is more or less completely polarised and the two doubly degenerate and perpendicular vibrations at 726 and 1389 are completely depolarised.

From the fact that the lines 726 and 697 possess different degrees of depolarisation they are to be considered as belonging to entirely independent vibrations and not as one line undergoing a change in frequency due to dilution. Thus there are eight remaining lines belonging to the undissociated nitric acid molecule. It has been pointed out by Dadieu and Kohlrausch that in agreement with Hantzsch's theory of pseudo-acids, the Raman spectrum of nitric acid gives evidence for the existence of the molecules in it having a form $HO.NO_2$. The structural formula should in that case be written as

(1)  or (2)  ·

In both forms the nitrogen atom can occupy a position either in the plane of the oxygen atoms as in the nitrate ion or at the apex of a pyramid. Thus if we assume that the strength of normal covalent bond between two atoms is different from that of a co-ordination bond between the same two atoms and neglect for a moment, the influence of the hydrogen atom, the first form of the molecule could be treated as $AB_2\,B'$ type and the second form as $AB\,B'B''$ type. E. B. Wilson[14] has calculated the number and the state of polarisation of the normal vibrations of these types on the basis of the selection rules for the Raman and the infra-red discussed by Placzek and has shown that there will appear six lines in both these types; but for the $AB_2\,B'$ type the depolarisation ratio will reach the limiting value of 6/7 for three of these lines if A is in the plane of the B atoms and for two lines if A is at the apex of a pyramid. For the $ABB'B''$ type where all the B atoms are dissimilar, only one of the lines will be completely depolarised if the molecule is plane and none at all if the molecule is pyramidal. In the nitric acid molecule besides these six normal vibrations, there should also be two lines belonging to the co-valent OH group, one of which is the valence oscillation

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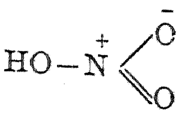
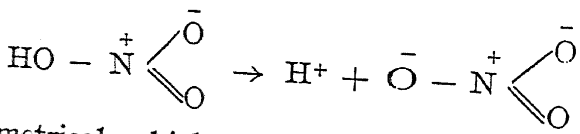
[13] Venkateswaran, S., *Phil. Mag.*, 1933, **15**, 263.

[14] Wilson, E. B. (Jr.), *Jour. Chem. Phys.*, 1934, **2**, 432.

which will be highly polarised and the other, the deformation oscillation which will be unpolarised. As indicated before in the concentrated solution of the acid these eight lines have been observed besides those due to the NO_3' ion, of which only one line at 1538 possesses a depolarisation ratio of 6/7. The line 1699 which has been reported for the $HO.NO_2$ molecule, possesses a low depolarisation ratio of less than 0·3 and is most probably wrongly assigned by Angus and Leckie to the 4358 radiations of the source.[15] The high degree of polarisation suggests that it is the valence oscillation of the hydroxyl group and its frequency shift is not 1699 but is 3466 cm.$^{-1}$ with 4046 as the exciting line, and is of the order of the OH frequency in the hydroxides and alcohols. The line 1538 which is weak and highly depolarised is also to be attributed to the deformation oscillation of the OH group.

All the other six remaining frequencies, namely, 638, 697, 924, 1126, 1297 and 1611, are polarised to some extent or other and therefore belong to a configuration AB_3 where all the B atoms are different and A is at the apex of a pyramid. Two of these frequencies, namely, $\omega_1 = 1297$ and $\omega_2 = 924$ which are the strongest of the group, are depolarised to an extent of only 0·30 and 0·17 respectively and are therefore due to the two parallel vibrations of the AB_3 type. The rest four are due to the four perpendicular vibrations.

Thus it is to be concluded that the nitric acid molecule has a structure  and that in the process of dissociation a great change takes place in the NO_3 group from a pyramidal to a plane equilateral type. If the plane structure were preserved in the undissociated molecule also, we could expect only a small change in the frequency shift of the parallel vibration of the NO_3 ion due to the ionisation of the hydroxyl group. The fact that the shift from $\omega_1 = 1297$ in the acid molecule to $\omega_1 = 1050$ in the ion is great, lends further support to the above conclusion. During the ionisation a simple process represented by  would make the nitrate ion unsymmetrical which is not supported by X-ray and Raman measurements. It is probable that the ionisation is accompanied by a rearrangement of electronic configuration of the nitrate group rendering the three oxygen atoms identical. Such a process may be

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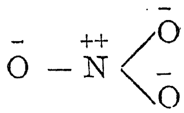
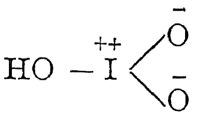
[15] Angus, W. R., and Leckie, A. H., *Proc. Roy. Soc.*, A, 1935, **149**, 327.

visualised by postulating that NO_3' ion is represented by  or that the double bond of one of the oxygen atoms is labile.

Iodic Acid.—For a 6 N solution of iodic acid the author has reported in a previous paper[16] five broad lines, namely, 330, 463, 644, 789 and 823. The band 789 is shown to be composed of two frequencies 789 and 796 and the band 330 of two lines at 328 and 377. Of these lines 789, 644, 463 and 330 are assigned to HIO_3 molecule, the line 823 to the polymerised ion I_2O_6'' and the line 796 to the IO_3' ion. The results given in Table II show that all these lines are polarised to varying degrees. The two lines possessing maximum polarisation are to be attributed to the two parallel vibrations of a pyramidal molecule of the form . The other lines 463 and 330 whose degree of depolarisation is higher probably belong to the perpendicular vibrations. Vibrations similar to the latter in nitric acid have a higher depolarisation ratio. It is probable that in the case of iodic acid, the depolarisation ratio of the 330 band is lowered by the presence of a parallel vibration belonging to the IO_3' ion in that region. The line at 823 which has been assigned to the polymerised radical I_2O_6'' also shows a high percentage of polarisation and therefore belongs to the symmetrical oscillations of that group.

It is interesting to observe that the frequency shift 789 corresponding to the parallel vibration in the iodic acid molecule suffers only very little change in passing to the iodate ion. This is partly due to the fact that in both states the molecular form remains pyramidal and partly due to the increased mass of the central atom.

Sulphuric Acid.—The early investigations of the Raman spectrum of this acid were of an unsatisfactory nature due to the presence of a strong fluorescence in the scattered radiations which masks all but the intense lines in the concentrated solutions. By oxidising the traces of organic impurities by a few drops of $KMnO_4$ or HNO_3 Médard[17] has been able to get rid of this fluorescence and to obtain a clear spectrum for the acid. By a similar method the author has obtained a fairly intense picture for 99% and 25% acid and the frequency shifts of the lines observed agree fairly well

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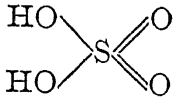
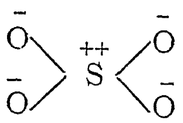
[16] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 119.

[17] Médard, L., *Compt. Rend.*, 1933, **197**, 582; 1934, **198**, 1407.

with those of Médard. In general, the 99% acid gives seven lines at 384-434 (4 br.), 564 (0), 916 (10), 970 (0), 1045 (4), 1140 (4 br.) and 1364 (0). Besides, a sharp line attributed to N_2O_5 also appears at 1398. Of these 384–434 shows a doublet structure which is confirmed further, by the different states of polarisation of the component parts. New lines that arise on diluting the acid with water are given in Table III(*b*).

According to classical literature, sulphuric acid is represented by the structural formula , where sulphur has sexavalency as in SF_6. The SO_4'' ion, formed after complete ionisation, possesses a symmetrical structure represented according to modern electronic conceptions as,  where all the four oxygen atoms are identical in agreement with the perfectly tetrahedral structure attributed to it. The mechanism of transition from the undissociated molecule to the dissociated SO_4'' ion is by no means clear.

The four frequencies which are present in the solutions of sulphates and attributed to the sulphate ion are 418, 597, 982 and 1168. Among the lines obtained for 25% acid, the intense line at 982 is more or less completely polarised and represents the symmetrical expansion and contraction of the perfectly tetrahedral SO_4'' ion. As is to be expected the other three degenerate frequencies 427, 593 and 1172, all belonging to the SO_4'' ion are depolarised more or less to an extent of 6/7.

The frequencies 384–434 and 564 appear to be common to the undissociated H_2SO_4 molecule and to the HSO_4' ion as well as to the SO_4'' ions.[18] Of the remaining frequencies cited in Table III, those at 916, 970, 1140 and 1364 belong to the undissociated molecule. If we assume that the latter is a distorted tetrahedron like CH_2Cl_2 with two oxygen atoms placed above sulphur and the two hydroxyl groups below, we can expect nine frequencies[19] in Raman effect of which five will be depolarised. The intense line at 916 shows a high degree of polarisation and evidently corresponds to the breathing frequency* of such a structure. As mentioned before, 384–434 is a doublet

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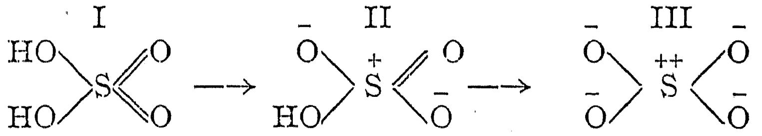
[18] Woodward and Horner, *Proc. Roy. Soc.*, A, 1934, **144**, 129.

[19] Wilson, E. B., *Loc. cit.*

* The term 'breathing frequency' in these pages refers to the vibration in which the tetrahedron contracts or expands as a whole.

and the ratio of depolarisation of the components is distinctly lower than 6/7. The broad line 1140 is also polarised. These four, thus, represent the polarised vibrations of the distorted tetrahedron. Three out of the five depolarised vibrations are 564, 970 and 1364 and the remaining two are probably too feeble to be recorded on the plate.

The lines which are known to belong definitely to HSO_4' ions are 1045, 1223 and 1334. Of these the most intense line at 1045 possesses a depolarisation ratio of about 0·24 and evidently corresponds to the expansion and contraction of the tetrahedron. It is interesting to observe that the depolarisation ratio of the breathing frequency which is almost zero in the SO_4'' ions is about 0·17 in the undissociated molecule and attains a value of more than 0·24 in the HSO_4' ions. If we assume that the extent of polarisation is a measure of the symmetry of structure of the molecular species, we are led to infer that HSO_4' ion is the most asymmetrical of the three. A mechanism which could satisfactorily explain these experimental results may be outlined as follows :—



The undissociated molecule having a structure given by formula I changes to form II after the first stage of ionisation and on further dissociation yields the symmetrical SO_4'' ion. The tetrahedral structure is preserved throughout ; but as may be easily seen the middle form representing HSO_4' ion has the least symmetry.

Selenic Acid.—In a detailed investigation of the Raman spectrum of selenic acid,[20] it has been pointed out that it behaves in Raman effect in a manner analogous to sulphuric acid and it is gratifying to note that the polarisation characters of the lines also correspond closely to that of the latter. The molten acid yields eight lines of frequency shifts 294 (3), 361 (6), 388 (6), 756 (10), 914 (8), 996 (3), 1105 (0) and 1186 (0). Of these 756, 996 388, 361 and 294 as well as 1105 and 1186 have been assigned to H_2SeO_4 molecule and 914 to the $HSeO_4'$ ion. If we assume the tetrahedral structure to H_2SeO_4 molecule and its dissociation products, the high degree of polarisation of 756 and 914 shows that they represent the symmetrical vibrations of H_2SeO_4 molecule and $HSeO_4'$ ion respectively. The polarisation characters of the other lines follow, in general, closely those of the corresponding

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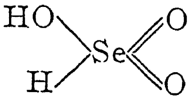
[20] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1936, 3, 307.

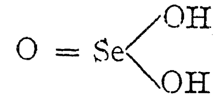
lines of sulphuric acid. But the greater asymmetry of the $HSeO_4'$ ion is not so clear as in the case of HSO_4' ion.

Selenious Acid.—The six frequencies reported previously[21] for the molten liquid are 238 (1), 343 (4), 380 (3), 545 (1), 690 (10) and 892 (10). The polarisation picture shows that the band 892 consists of two components with frequency shifts of 862 and 910 and are, therefore, listed separately in Table V. The broad lines 343 and 380 show a depolarisation of 6/7 and hence confirm their assignment to the lower degenerate vibrations of the molecular species which are assumed to possess a pyramidal structure. The line 545 is attributed to the unsymmetrical form



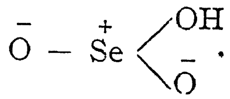
$\begin{matrix}HO\\H\end{matrix}\!>\!Se\!<\!\begin{matrix}O\\O\end{matrix}$

and the line 690 to the symmetrical form



$O=Se\!<\!\begin{matrix}OH\\OH\end{matrix}$.

Both these lines are polarised indicating that they correspond to the vibrations having maximum symmetry in the respective molecules; but their relative degree of depolarisation could not be determined due to the extreme feebleness of the line 545 in the molten liquid. The high degree of polarisation of 862 shows that $HSeO_3'$ ion is more symmetrical than the undissociated molecule and is, therefore, probably more accurately represented by the formula

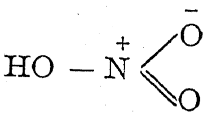


$\overset{-}{O}-\overset{+}{Se}\!<\!\begin{matrix}OH\\ \overset{-}{O}\end{matrix}$.

In conclusion the author wishes to express his heartfelt thanks to his professor Sir C. V. Raman for his constant interest in the work.

Summary.

The polarisation of Raman lines of nitric, iodic, sulphuric, selenic and selenious acids is investigated making use of the usual double-image prism method. All the lines of the concentrated nitric acid except one at 1538 which is attributed to the deformation oscillation of the hydroxyl group, show varying degrees of depolarisation which are less than the limiting value 6/7. The lines due to the nitrate ion possess a state of polarisation which is in agreement with the plane equilateral structure attributed to it. From the results of polarisation six lines belonging to the undissociated nitric acid molecule are identified with the known modes of oscillation of an unsymmetrical pyramidal model having a structure



$HO-\overset{+}{N}\!<\!\begin{matrix}\overset{-}{O}\\O\end{matrix}$.

The

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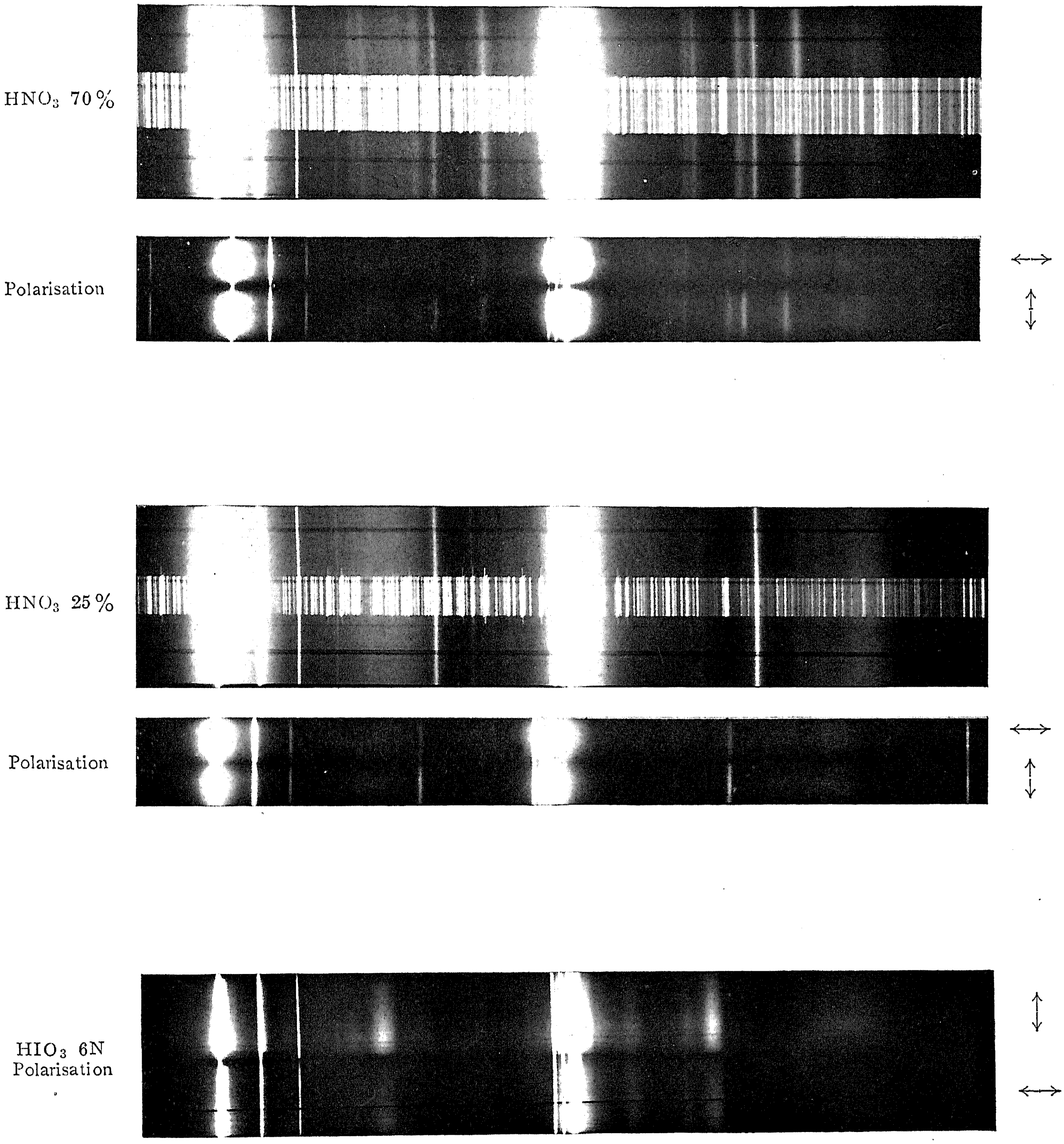
[21] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1936, 3, 533.

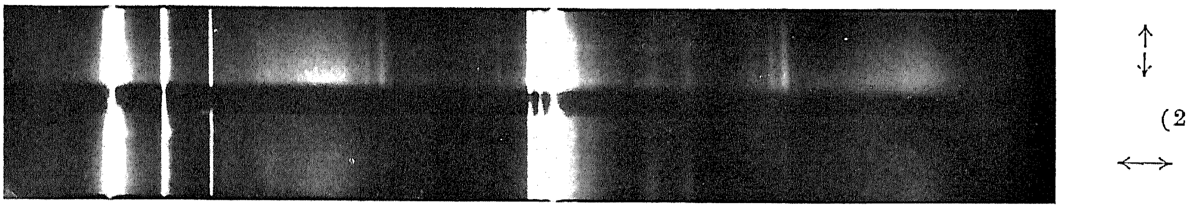


Raman Spectra—Polarisation

H_2SO_4 99 %
Polarisation

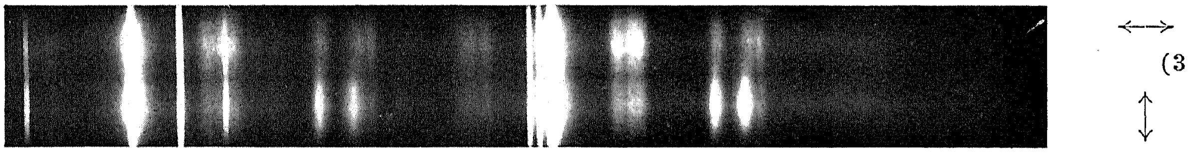
(1)

H_2SO_4 25 %
Polarisation



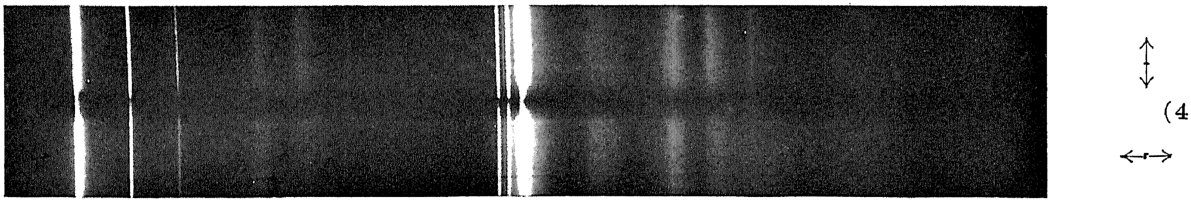
(2)

H_2SeO_4
molten
Polarisation



(3)

H_2SeO_3
molten
Polarisation



(4)

Raman Spectra—Polarisation

state of polarisation of the Raman lines of the H_2SO_4 molecule and its dissociation products, HSO_4' and SO_4'' ions generally supports the assumption that all the three forms are tetrahedral and that HSO_4' ion is the most distorted of the three. Structural formulæ of the three species and the mechanism of dissociation from one form to the other are discussed in relation to the degree of depolarisation of the breathing frequency. Polarisation of the Raman lines of selenic acid is analogous to those of sulphuric acid. The results of polarisation of the bands of iodic acid as well as selenious acid generally support the previous assignments of these bands to different molecular species.