

# THE RAMAN SPECTRUM AND ELECTROLYTIC DISSOCIATION OF SELENIC ACID.

BY C. S. VENKATESWARAN.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received March 26, 1936.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

## 1. Introduction.

IN the previous communications to these *Proceedings*<sup>1</sup> the author has shown how a detailed study of the Raman spectra of weak acids like iodic and phosphoric acids yield information regarding the progressive electrolytic dissociation of these acids in aqueous solutions. The present paper deals with the results obtained in a similar investigation with selenic acid. The Raman spectrum of a strong solution of this acid has been studied by A. S. Ganesan<sup>2</sup> and he has reported five lines of frequency shifts\* 315 (*m*), 422 (*m*), 730 (*f*), 850 (*s*), 926 (*f*) which differ in a marked manner from the shifts of the modified lines in selenates. A quantitative study of the Raman spectrum of this acid for a wide range of concentrations and a comparison of the results with those of sulphuric acid appear to be of great interest; for it could be expected to yield some information regarding the properties of similar compounds belonging to the same homologous series in the periodic system. The Raman spectra studies of sulphuric acid are numerous and though the results are vitiated to some extent by the presence of a strong continuous spectrum, there is general agreement among the several investigators regarding the evidence for the stepwise dissociation of this acid. In the case of selenic acid, as far as the author is aware of, there are no physico-chemical data available at present indicating its stages of ionisation. It can also be easily obtained in the crystalline form in which it exists as hundred per cent acid and it possesses a low melting point of about 50°.8 C. Hence it affords an interesting case of an acid in which the changes in position and character of the Raman lines could be followed up as it passes from solid to liquid and to solutions of varying concentration and the manner of electrolytic dissociation could be uniquely determined.

<sup>1</sup> Venkateswaran, C. S., *Proc. Ind. Acad. Sci., A*, 1935, 2, 119; 1936, 3, 25.

<sup>2</sup> Ganesan, A. S., *Proc. Ind. Acad. Sci., A*, 1934, 1, 156.

\* The numbers in this and the subsequent pages denote the wavenumbers in  $\text{cm}^{-1}$ .

### 2. *Experimental.*

The experimental set up for this investigation was the same as those described by the author in the previous communications.<sup>3,4</sup> Hundred grams of pure crystalline selenic acid were supplied by Kahlbaum in a sealed tube and were used as such without further purification. Since the substance is highly hygroscopic, the sealed tube was kept intact during the investigation in the solid, molten and super-cooled states. The time of exposure for obtaining a satisfactory spectrogram was half an hour for the solid and twenty-four hours for the molten and the super-cooled liquid. In order to obtain a fairly quantitative estimate of the relative intensities of the lines in the aqueous solutions of varying concentration the product of the concentration and the time of exposure was kept constant, while the other conditions of experiment remained the same. The time of exposure for the 92.5% solution was twelve hours and was correspondingly increased for other concentrations. Specially backed Ilford "Golden Isozenith" plates were used for photographing the spectra. The plates were measured by means of a Hilger cross-slide microscope in comparison with an ion arc spectrum which was recorded in the centre of every picture.

### 3. *Results.*

Enlarged photographs of the spectra are reproduced in the accompanying plates and illustrate the changes in the Raman lines during the transition from solid to liquid and to the aqueous solutions. The concentrations are given as percentages of the solid per hundred grams of the solution. The schematic representation of lines in Fig. 1 shows clearly the changes in position and relative intensities of the lines as the dilution progresses. The thick dark lines are drawn with reference to a frequency scale in  $\text{cm.}^{-1}$  units and their positions in the scale represent the frequency shifts corresponding to the maximum intensity of the banded Raman lines. The height of each dark line is proportional to the intensity of the corresponding modified line. The lines due to the same mode of vibration of the molecule in the different stages of dilution are joined together by dotted lines and their assignment is indicated below.

<sup>3</sup> Venkateswaran, C. S., *Proc. Ind. Acad. Sci., A*, 1935, 1, 850; *loc. cit.*

<sup>4</sup> Venkateswaran, C. S., *Proc. Ind. Acad. Sci., A*, 1936, 3, 25.

TABLE I. (Selenic acid.)  
Raman frequencies in  $\text{cm}^{-1}$ .

State of Substance	1	2	3	4	5	6	7	8	9	10	11	12
Crystal	.. 1383 (1)	..	930 (1) sh.	..	..	896 (5) sh.	..	778 (1)	766 (5) sh.	374 (2) sh.	355 (1) sh.	327 (1) sh.
Molten	..	1186 } (0) 1105 }	996 (3) 36	..	..	914 (8) 70	..	..	756 (10) 70	388 (6) 40	361 (6) 40	294 (3) 40
Super-cooled	..	..	978 (2) 32	..	..	899 (8) 30	..	..	752 (10) 30	387 (3) 16	360 (3) 16	294 (3) 20
92.5	..	1160 (0) band	975 (1) 12	927 (2) 16	..	862 (5) 20	..	..	747 (10) 30	..	374 (5) 60	299 (5) 30
75	..	..	..	934 (3) 20	..	826 (8) 16	..	..	748 (6) 20	..	390 (3) 50	307 (4) 30
50	..	..	..	929 (3)	..	862 (10) 16	845 (0) sh.	..	742 (3) 20	..	390 (3) 40	312 (3) 30
30	..	..	..	929 (2)	910 (0)	866 (10)	846 (1)	..	737 (3) 20	..	390 (3) 30	327 (3) 30
20	..	..	..	925 (2)	908 (2)	866 (8)	845 (2)	..	732 (2) 20	..	398 (3) 20	332 (3) 20
15	..	..	..	921 (1)	908 (2)	866 (8)	845 (4)	..	732 (1) 20	..	400 (3) 16	332 (3) 20
7.5	..	..	..	921 (0)	908 (1)	866 (6)	845 (3)	..	732 (0) 20	..	402 (1) 16	332 (1) 20

Note.—The numbers within the brackets indicate visual estimate of intensities and the numbers below each frequency give the breadth of the line in  $\text{cm}^{-1}$ .

Table I gives the frequency shifts of the centre of the Raman lines of the acid as solid, liquid and aqueous solutions of concentrations ranging from 92.5% to 7.5% by weight. Visual estimates of the intensities of the lines are given within brackets accompanying the corresponding line. The extension of the line to either side of its centre is given in wavenumber units below the frequency values.

#### 4. Discussion of Results.

The Raman spectrum of the crystalline selenic acid consists of seven sharp lines of frequencies 930 ( $\frac{1}{2}$ ), 896 (5), 778 (1), 766 (5), 374 (2), 355 (1)

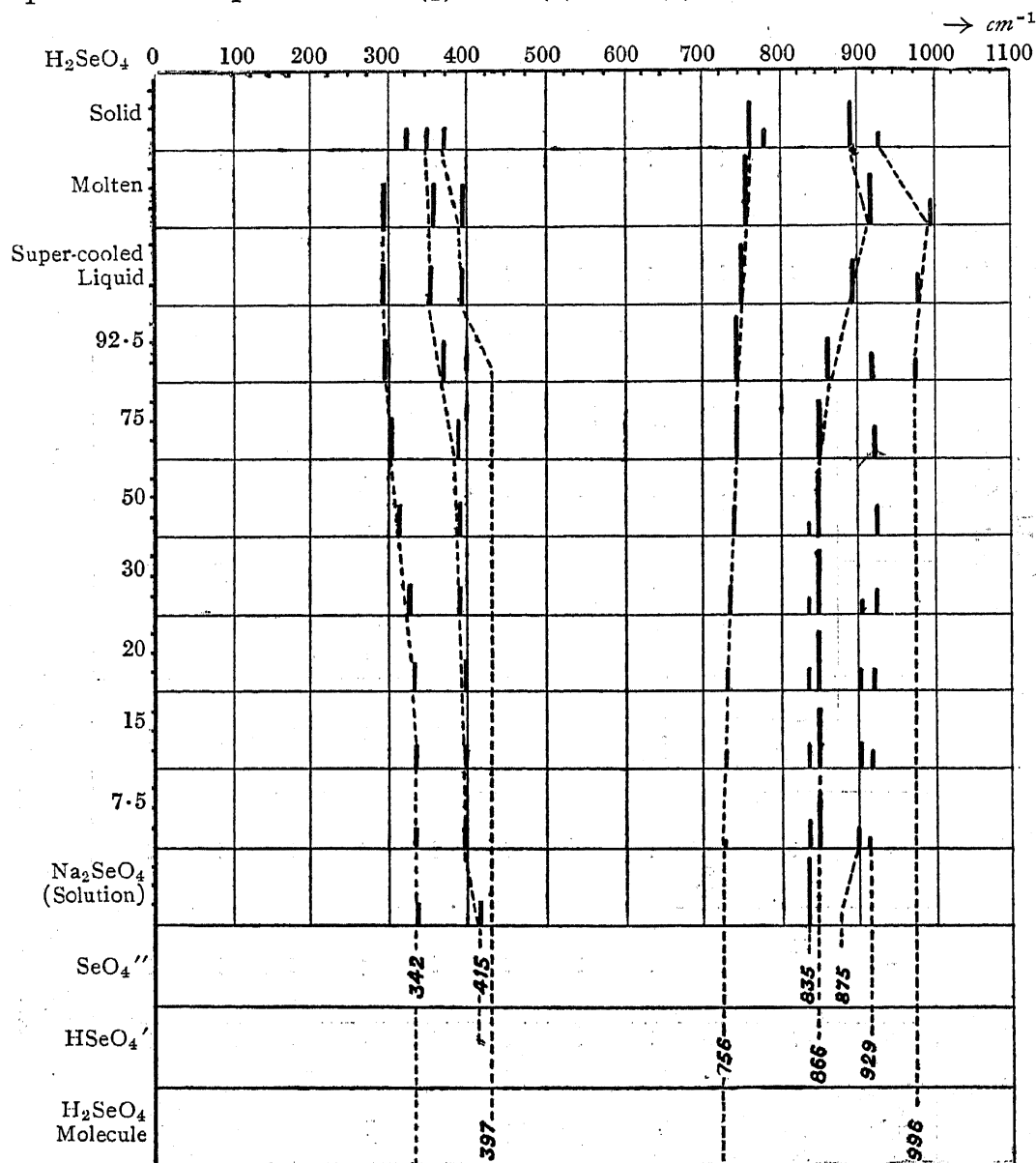


FIG. 1.

and 327 (1). Though the slit width employed throughout the experiment was a minimum (about 1/50 mm.), all the lines in the solid broaden out in the liquid and the solutions of high concentrations and tend to become sharper as the dilution increases. The lines undergo relative positional changes as can be inferred from the dotted lines indicating the course of each line in Fig. 1.

On melting the solid, the weak line 930 becomes a band of about 36 wavenumbers in width and undergoes a maximum shift of 66 wavenumbers towards higher frequency. In the super-cooled liquid this line as well as the other lines tend to approach that of the solid. The addition of a small quantity of water to the acid diminishes its intensity considerably and the frequency shift is also less than in the liquid state. At 75% this line practically disappears. But, instead, a new band makes its appearance first at 92.5% with a frequency shift of about 927 and increases in intensity from 92.5% to 30%. The centre of the line undergoes a gradual shift towards shorter frequency as dilution increases. At about 30% concentration this band at 927 shows a distinct doublet structure and for the lower concentrations it shows a clear asymmetry in intensity, the shorter frequency side increasing and the longer frequency side decreasing gradually in intensity. This is interpreted as due to the appearance of a new line at 910 at about 30% concentration, which is probably also present weakly at higher concentrations and which accounts for the apparent frequency shift of the line. The new line at 910 possesses a fairly constant frequency.

The line 896 which is one of the two intense lines in the solid phase has a finite breadth, but becomes very much broader (about 70 wavenumbers) and shifts towards a higher frequency of 914 in the liquid. The structure of this band is, however, different from that of the rest in the spectrum. It consists of a fairly broad line of maximum intensity at the centre and followed on either side by rotation wings. On the addition of water this line undergoes a marked change both in structure and position. In the 92.5% solution, it has only a breadth of about 20 wavenumbers. The frequency corresponding to maximum intensity is 862, thus undergoing a change of about 50 wavenumbers towards shorter frequency from the liquid to the solution. It has a constant frequency at all dilutions and becomes sharper at lower concentrations. The changes of intensity of this line are very striking. At 92.5% it is only half as intense as the one at 747; but at 75% its intensity is already slightly greater than that of the latter and goes on increasing up to about 30%. Though it continues to be the most intense line at lower concentrations, it appears to lose in intensity on further dilution. At

about 30% a new sharp line begins to make its appearance at 845 and gains in intensity as the dilution progresses.

The intense line at 766 and its faint companion at 778 of the solid appear as a single broad line (about 70 wavenumbers) in the molten state as well as at all dilutions. But this band changes in position progressively towards smaller frequency both during the transition from the solid to the liquid and on the addition of more and more of water. It appears as the most intense line in the liquid and in the solution of 92.5% concentration; but rapidly loses its intensity with dilution. At about 7.5% it is very faint and difficult to measure though it remains fairly broad. The extraordinary breadth of this line even at the highest dilution can be interpreted as due to the superposition of two diffuse lines, which in the solid show themselves as sharp lines. The change in the relative intensities of the two components also probably account to some extent for the frequency changes of the band towards the stronger line.

The two low frequencies at 274 and 355 in the solid state preserve the doublet character in the molten liquid, but in the solution appear as a single broad band (about 60 wavenumbers) which is asymmetrical in structure, being more intense towards shorter wavelength. The changes in the asymmetry of its structure in the solutions, however, show that the higher frequency component diminishes rapidly in intensity. The third low frequency at 327 in the solid, on the other hand, undergoes a degradation in frequency from the solid to liquid and becomes broad. It has almost the same frequency value at 92.5% solution as in liquid, but gradually increases towards higher frequency as the dilution progresses in the same manner as the band at 390. Though up to about 50% concentration the 390 band is broader than the one at 312, they are almost equal at 30% and at lower concentrations, there is a complete reversal in the relation between the widths of these two bands.

TABLE II. (Sulphuric acid.)  
Raman frequencies in  $\text{cm}^{-1}$ .

Concentration	1	2	3	4	5	6	7	8	9
100%	..	562	911 (6) 30	..	..	..	1142	..	..
90%	408 (3) 60	565 (4) 60	911 (5) 35	970 (0)	..	1038 (4) 40	..	..	..
75%	418 (3) 60	579 (4) 60	905 (4) 40	..	..	1034 (5) 40	..	..	..
50%	426 (3) 60	588 (4) 60	897 (3) 50	..	982 (2) 20	1038 (5) 40	1172	1234	1341
30%	427 (3) 60	593 (4) 60	896 (2) 55	..	982 (6) 20	1047 (6) 30	1172	1223	1334
20%	429 (3) 60	592 (4) 60	895 (0) 60	..	983 (0) 20	1050 (6) 25	1168	1236	faint
10%	faint	592 (4) 60	895 (0) 60	..	983 (6) 20	1051 (6) 20	..	..	..

Besides these lines there is one line at 1383 in the solid and two diffuse lines at 1186 and 1105 in the liquid which appear as a broad band at 92.5% concentration.

The characteristic Raman band of water begins to show at 75% and gains rapidly in intensity as the dilution progresses. The triple structure of the band is difficult to identify but the relative intensities of the different portions of the unsymmetrical band agree fairly closely with that of pure water itself.

#### 5. Comparison with Sulphuric Acid.

It is known that selenic acid is a strong acid comparable in strength with its analogue, sulphuric acid and it is to be expected that it should show an anomalous behaviour in its Raman spectra similar to that of the latter. The above picture of the changes in position, intensity and structure of the Raman lines, corresponds closely with similar observations by previous investigators<sup>5</sup> in sulphuric acid. For purposes of comparison the Raman frequencies of sulphuric acid solutions are reproduced in Table II from an exhaustive study of this acid by Bell and Jeppesen.<sup>6</sup> In general, the Raman spectra of the different solutions of this acid consists of four sets of lines namely,

(1) 911-895 and 1142 which are present in the 100% acid and drop off in intensity as it is diluted; these are assigned to the undissociated molecules.

(2) 1038-1051 which is not present in the pure acid but which appears and rapidly becomes stronger on dilution; this is attributed to  $\text{HSO}_4'$  ions.

(3) 982 which though present in 50% and perhaps also in 75% becomes appreciable only at concentrations lower than 25%; this is characteristic of the  $\text{SO}_4''$  ions.

(4) Those at 408-429 and 562-592 which are present at all concentrations and seem to belong to the ions and molecules alike.

Our results with selenic acid can also be classified as above.

(1) The lines 756-732, 996-976, 388-397 and 1186-1160 are present in the liquid and in 92.5% solution, but either totally disappear or drop off in intensity as the dilution increases. It is interesting to observe that the most intense line in this group, namely, 756-732 undergoes a shift towards a lower frequency just as the corresponding line 911-895 in the sulphuric acid.

(2) The lines 862 and 927-921 rapidly increase in intensity up to about 30% and remain intense throughout.

<sup>5</sup> For complete references, see Angus and Leckie, *P.R.S.*, 1934, 149A, 327.

<sup>6</sup> Bell, R. M., and Jeppesen, M. A., *J. Chem. Phys.*, 1935, 3, 245.



(3) The lines 908 and 845 begin to appear faintly at about 50% and increase in intensity on further dilution. Unlike the corresponding line 982 of sulphuric acid, the line 845 never becomes a prominent line in the spectrum.

(4) The broad lines 360-402 and 294-332 are present at all concentrations as well as in the solid. They behave exactly like the lines 562-592 and 408-429 in sulphuric acid as regards positional changes.

There is, thus a close correspondence between the two spectra, the corresponding frequencies themselves being smaller in selenic acid as is to be expected because of the greater atomic weight of selenium.

Recently there has been a controversy regarding the frequency shifts of some of the lines in sulphuric acid. Woodward and Horner<sup>7</sup> have pointed out that the apparent shifts could be interpreted on the basis that the broad lines consist of components of slightly different frequencies which appear and disappear at different concentrations. Bell and Jeppesen,<sup>8</sup> however, disagree with the above authors and insist that the lines are symmetrical, and the shift is gradual and depends on the influence of the state of solution on the vibrations of the molecular species concerned.

As has been pointed out before, our results with selenic acid support the view put forward by Woodward and Horner regarding the composite nature of the broad lines. The bands in the selenic acid which undergo frequency variations show a doublet nature at a particular concentration and a marked asymmetry in their structure at other dilutions. In the solid, the corresponding lines are generally split up. The only exception to this is the low frequency at about 300. These observations were possible in the spectra of this acid because of the clearness of the picture in all states. But in the case of sulphuric acid, a strong continuous spectrum obscures finer details. In view of the close accord between the results of selenic acid and sulphuric acid in other respects, it seems probable that in the case of the latter also the diffuse Raman lines consist of relatively narrow components as suggested by Woodward and Horner. It should, however, be pointed out that the complete drift of the lines due to changing concentrations could not be accounted for mainly on the basis of components.

#### 6. *Electrolytic Dissociation of Selenic Acid.*

From what has been stated in the previous section, it will be clear that the anomalous variation in intensity and frequency shifts that are observed in the Raman lines in selenic acid could be explained in the same manner as in the case of sulphuric acid, namely, by assuming that this acid, like the

<sup>7</sup> Woodward and Horner, *Proc. Roy. Soc., A*, 1934, 144, 129.

<sup>8</sup> Bell, R. M., and Jeppesen, M. A., *loc. cit.*

latter ionises in two stages, first from  $\text{H}_2\text{SeO}_4 \rightarrow \text{HSeO}_4' + \text{H}^\circ$  and then from  $\text{HSeO}_4' \rightarrow \text{SeO}_4'' + \text{H}^\circ$ . On the basis of this hypothesis the band 756–732 which is prominent in the molten condition and falls off in intensity gradually in aqueous solutions, is characteristic of the undissociated molecules. The lines with frequency shifts of 1186, 1105, 996–976 and 388 which are present only at 100% liquid and 92.5% solution also arise from the  $\text{H}_2\text{SeO}_4$  molecules. The second intense line at 862 which gains rapidly in intensity as the concentration falls from 92.5% to 30% and the line at 927 are to be attributed to the first ionisation product,  $\text{HSeO}_4'$  ions. The frequency shifts observed for  $\text{KHSeO}_4$ <sup>9</sup> are 852 and 339. The close agreement between the line 852 in the biselenate and 862 assigned to  $\text{HSeO}_4'$  ion lends support to the above conclusion. Its presence in the 100% acid shows that, as is not the case with sulphuric acid, a certain proportion of molecules in the solid and the liquid states has undergone partial dissociation from  $\text{H}_2\text{SeO}_4$  to  $\text{HSeO}_4'$ . The great intensity of this line in most of the concentrations is due to the preponderance over all others of the  $\text{HSeO}_4$  ions which give rise to it and shows its remarkable stability in the aqueous solutions. The line at 845 which makes its appearance first at 50% and gains steadily in intensity on further dilution, as well as the line at 908 are to be attributed to the normal vibrations of the  $\text{SeO}_4''$  ions. This indicates that the second stage of ionisation from  $\text{HSeO}_4' \rightarrow \text{SeO}_4'' + \text{H}^\circ$  begins only at 50% and even at 7.5% it is not appreciable. The two low frequencies 361–402 and 294–332 appear to be common to all the three molecular species.

In Table III the frequencies assigned to  $\text{SeO}_4''$  and  $\text{SO}_4''$  ions in the acids are compared with the corresponding frequencies in selenates<sup>10</sup> and sulphates<sup>11</sup> respectively.

TABLE III.

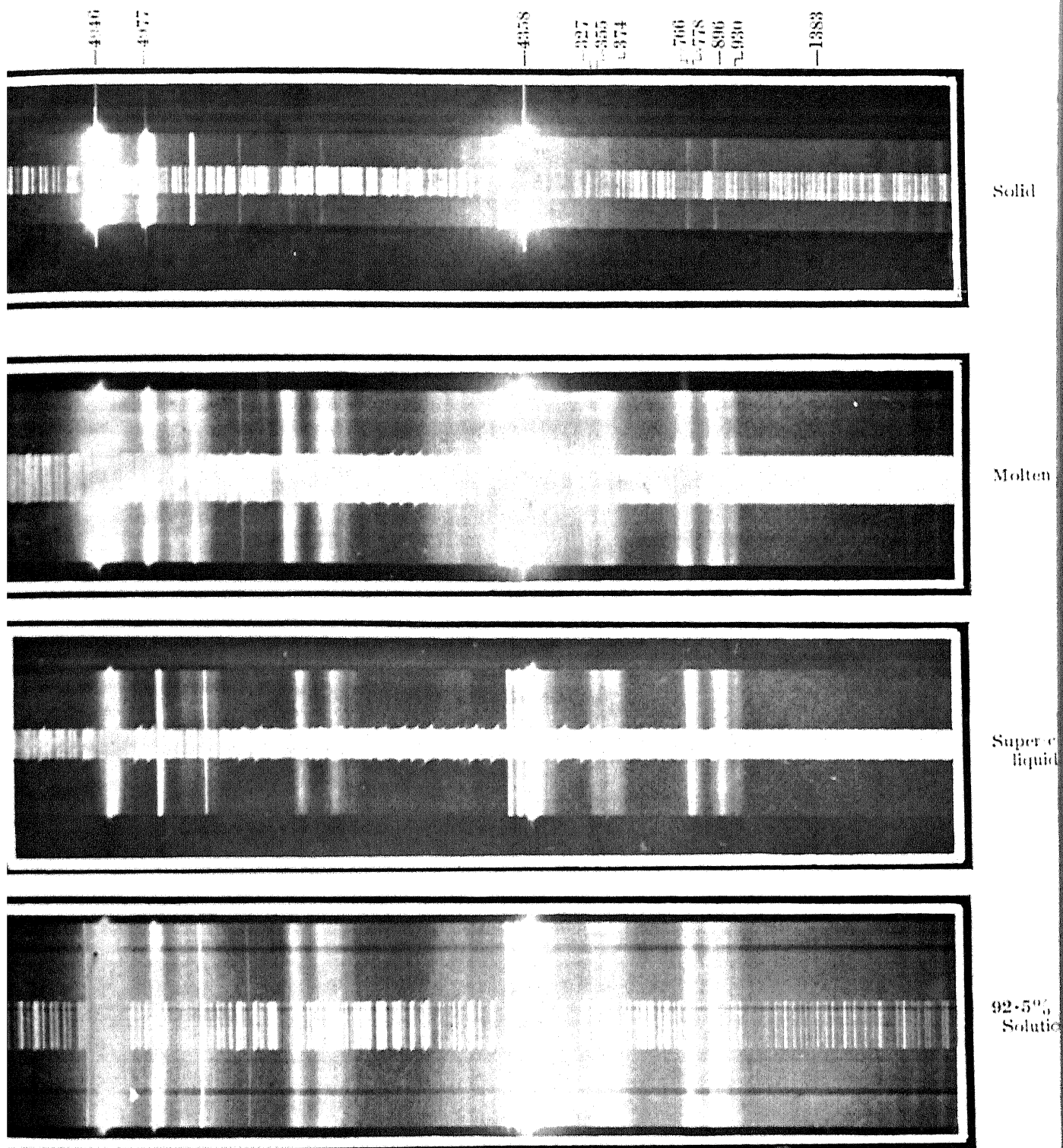
$\text{SeO}_4''$ (in 7.5% acid)	..	332	402	845	908
$\text{SeO}_4''$ (in Selenate)	..	342	415	835	875
$\text{SO}_4''$ (in 10% acid)	..	418	597	982	1168
$\text{SO}_4''$ (in Sulphate) <sup>o</sup>	..	447	623	983	1115

It is interesting to note a systematic variation in frequencies in both  $\text{SeO}_4''$  and  $\text{SO}_4''$  ions while passing from the acid to the salt. The close agreement between the values of the Raman lines arising from  $\text{SeO}_4''$  in the acid and the selenates, lends support to the above interpretation of the results. The

<sup>9</sup> Pringsheim and Yost, *Zeit. f. Physik*, 1929, 58, 1.

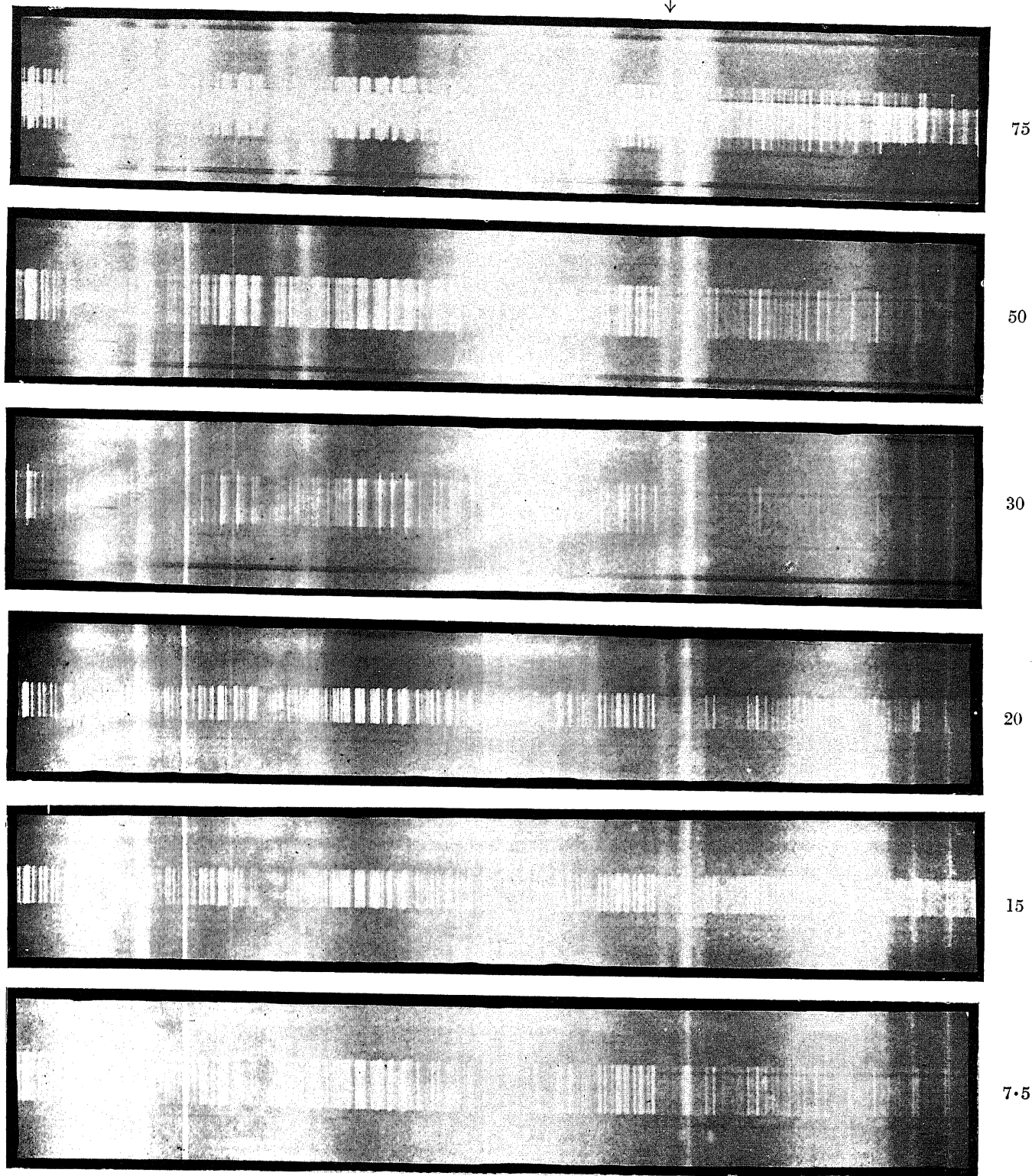
<sup>10</sup> A. S. Ganesan, *loc. cit.*

<sup>11</sup> Kohlrausch, *Der Smekal-Raman Effect*, 1931.



Raman Spectra of Selenic Acid  
(Solid, Liquid and Solution).

← 748



Raman Spectra of Selenic Acid Solutions.

↑ 845      ↑ Water band

presence of the line at 732 even at 7.5% solution shows that a certain proportion of the  $\text{H}_2\text{SeO}_4$  molecules exists even at those dilutions. It is very difficult to say whether the  $\text{SeO}_4''$  ions are produced by the direct dissociation of  $\text{H}_2\text{SeO}_4$  to  $2\text{H}^\circ$  and  $\text{SeO}_4''$  or only from the first ionisation product  $\text{HSeO}_4'$  which appears to be very stable. In general, the results indicate that selenic acid possesses a lower degree of ionisation than sulphuric acid.

The absence of any line in the spectrum of selenic acid at about 2312 corresponding to the Raman line in liquid hydrogen selenide<sup>12</sup> signifies that no H-Se bond is present in the molecule.

#### 7. *Change of State and Raman Effect.*

The influence of change of state from the solid to liquid on the Raman lines of this acid is illustrated in the accompanying plate. Two distinct changes occur on the lines, namely, a shift towards longer wavelength of all the lines except 766 and 327 which have a reverse effect and a general broadening. In the super-cooled liquid these effects are, to some extent, less pronounced. In general, these changes of the lines following the change of state are characteristic of hetro-polar compounds.<sup>13</sup> Their full significance will be discussed in a separate paper along with the results of selenious acid.\*

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

#### *Summary.*

The Raman spectrum of selenic acid has been investigated in the state of solid, liquid and aqueous solutions of concentrations varying from 92.5% to 7.5% by weight. The solid has yielded eight lines with frequency values of 1383, 930, 896, 778, 766, 374, 355 and 327. Marked changes in position, intensity and character of these lines are observed during the transition from the solid to the liquid and then to the aqueous solutions. The gradual disappearance of some of the lines and the increase in the intensity of some others and the appearance of new lines are explained on the basis of the stepwise dissociation of the acid, namely,  $\text{H}_2\text{SeO}_4 \rightarrow \text{HSeO}_4' + \text{H}^\circ$  and  $\text{HSeO}_4' \rightarrow \text{SeO}_4'' + \text{H}^\circ$ . The results indicate that the first stage of ionisation starts from the solid and the second stage from about 50% concentration. The results are compared with those of its analogue, sulphuric acid and conclusions are drawn regarding the structure and the apparent shifts of the bands in both these acids. The changes that take place in the lines during the transition from the solid to the liquid are characteristic of the hetro-polar nature of the chemical bond in the acid molecules.

<sup>12</sup> Dadiou and Engler, *Wien Ans.*, 1935.

<sup>13</sup> Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, 2, 260.

\* Unpublished work of the author.