THE RAMAN SPECTRA OF SELENIOUS ACID AND ITS SODIUM SALTS.

By C. S. Venkateswaran.
(*From the Department of Physics, Indian Institute of Science, Bangalore.*)

Received May 28, 1936.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction.*

Recently in a note to *Current Science*[1] the author published the preliminary results of an investigation on the Raman spectrum of crystalline selenious acid. Then it was pointed out that the spectrum of the solid consists of not less than twelve sharp lines and is essentially different from that of its aqueous solution which has been reported on by Pringsheim and Yost.[2] To understand fully the significance of these lines in the solid, a detailed study of the problem has been undertaken and this report presents the results obtained both with the acid in the solid and molten states and in aqueous and alcoholic solutions and with the selenite and biselenite of sodium.

2. *Experimental Method and Results.*

The experimental procedure was the same as has been described in the previous communications to these *Proceedings*. The substance used in this investigation was the anhydrous acid supplied by Kahlbaum. Fresh selenious acid prepared by the oxidation of selenium with concentrated nitric acid and purified by repeated recrystallisations from water gave an identical spectrum. The anhydrous acid shows a marked tendency to decompose on heating but the hydrated variety melts at about 70° C. to a light yellow liquid. For all purposes, this liquid is to be considered only as a solution of H_2SeO_3 in its water of crystallisation. It gave an intense spectrum with the 4358 radiations of the mercury arc; but the 4047 line of the source was partially absorbed. The separation of amorphous selenium due to the action of light on the acid in the aqueous and alcoholic solutions gave rise to increased Tyndall scattering; yet tolerably good pictures were obtained by carefully filtering the solutions several times through thick folds of filter paper.

---

[1] Venkateswaran, C. S., *Current Science*, 1935, **4**, 309.

[2] Pringsheim and Yost, *Z. Physik*, 1929, **58**, 1.

The biselenite of sodium was prepared by titrating with a solution of sodium hydroxide using *p*-nitrophenol as indicator and the selenite by using thymolphthalein as indicator.

The spectrograms were measured by means of a Hilger Cross-slide microscope in comparison with an iron arc spectrum. The results are given in Tables I, II and III and the enlarged photographs of some of the spectra are reproduced in the accompanying plate.

TABLE I.

H_2SeO_3 *Crystal.* (d = 4047, e = 4077 *and* h = 4358.)

No.	Raman lines		$\Delta\nu$ cm.$^{-1}$	Intensity	Assignment
	wave-length	wave-number			
1	4047·0	24581	124	2	*d*
2	4088·3	24453	252	4	*d*
3	4094·0	24418	287	2	*d*
4	4096·0	24407	298	1	*d*
5	4107·0	24342	363	0	*d*
6	4120·5	24262	254	2	*e*
7	4126·1	24229	287	0	*e*
8	4134·5	24180	528	3*br*	*d*
9	4146·8	24108	597	8	*d*
10	4166·1	23996	709	3	*d*
11	4179·4	23920	596	3	*e*
12	4197·3	23818	887	8	*d*
13	4195·9	23826	888	1	*h*
14	4201·1	23796	909	2	*d*
15	4206·9	23764	941	1	*d*
16	4231·4	23626	890	2	*e*
17	4246·4	23543	605	2	*h*
18	4303·9	23228	290	1	*h*
19	4311·6	23187	249	2	*h*
20	4321·9	23132	194	1	*h*
21	4396·5	22739	199	3	*h*
22	4407·3	22683	255	6	*h*
23	4415·9	22639	299	2	*h*
24	4428·7	22574	364	0	*h*
25	4460·3	22414	524	3	*h*
26	4475·0	22340	598	8	*h*
27	4496·6	22234	704	3	*h*
28	4528·6	22076	862	0	*h*
29	4534·0	22049	889	10	*h*
30	4538·2	22029	909	2	*h*
31	4544·6	21998	940	0	*h*

R. lines = $1\overline{24}$(2), $1\overline{99}$(3), $2\overline{5}4$(6), 287(2), $2\overline{99}$(2), 364(0), 524(3), $5\overline{9}7$(8), 706(3), 862(0), $8\breve{8}9$(10), 909(2), 940(0).

TABLE II.

(Raman Frequencies in cm.$^{-1}$) H_2SeO_3 (Aqueous and Alcoholic Solutions.)

Solid 30° C.	Molten 70° C	Aqueous solutions					Solution in MeOH		Aq. Soln. (Pringsheim and Yost)
		60 %	40 %	30 %	15 %	7·5 %	40 %	15 %	
124(1)									
199(3)									
254(6)	238(1)								
287(1)									
299(2)	343(4)	355(2) diff.	355(2)	355(1)	355(1)	..			
364(0)	380(3)								
524(3)									
	545(1) broad	528(0)	528(0)	528(0)	528(0)	..			
597(8)	..	..	..	..	..	..	589(*m*) (*br*)	589(*m*) (*br*)	..
706(3)	690(10) ± 30	695(6) ± 25	695(6) ± 25	695(6) ± 25	695(6) ± 20	695(6) ± 20	..	..	695
862(0)									
889(10)	892(10) ± 50 (Max. at 862)	895(6) ± 30	900(6) ± 25	906(6) ± 20	906(6) ± 15	910(6)	930(*m*)	935(*m*)	885
909(2)									
940(0)									

TABLE III.

Raman Frequencies of Sodium Salts. Exciting line 4358 ·3 A.U.

Substance	Raman lines		Δ ν in cm.$^{-1}$	Intensity	Previous work
	Wave-length A.U.	Wave-number			
Na H SeO_3 15 % Aq. Solution	4423 ·0	22603	335	1 (diff.)	339
	4476 ·0	22335	603	1 (diff.)	..
	4527·5	22076	862	5	853
Na_2 SeO_3 10% Aq. Solution	4430·8	22563	375	1 (diff)	nil
	4475 ·0	22340	598	0 (?)	
	4502·5	22204	734	1 (*sh*)	
	4517 ·1	22132	806	5	
	4527 ·5	22076	862	5	

3. *Discussion of Results.*

The crystalline acid has yielded a spectrum which is very rich in lines, all of which are sharp and well defined. These lines may be divided into five groups, namely, (1) 889 and three companions at 860, 909 and 940, (2) 706, (3) 597 and its companion at 524, (4) 287, 299 and 364 and (5) 124, 199 and 254. Of these lines, the five low frequencies as well as the strong lines 597 and 889 have yielded their antistokes. On melting the solid, all the lines of the first group merge together into one strong broad band with its centre at 892. It is definitely asymmetrical in structure and its maximum intensity is at 862.* The centre of this band shifts to a longer wave-length as the concentration of the solution falls off. Its breadth also gradually diminishes. In the alcoholic solution the shift is distinctly greater than in the aqueous solution of the same concentration by about 30 wave-numbers.

The most remarkable change takes place in the relative intensities of the second and the third group of lines. While in the solid the line at 706 is only of *medium intensity*, in the molten liquid as well as in the aqueous solutions of all concentrations it is the *strongest line* in the spectrum. Its frequency shift is also smaller by about 10 wave-numbers. This line does not at all appear in the alcoholic solutions. On the other hand, the strong line 597 of the solid appears as a faint line at 545 with a finite width in the molten state. The faint satellite 524 of this line is also probably merged into the 545 line of the solution. In the alcoholic solutions, it is the most intense line in the spectrum ; but undergoes a distinct lowering of frequency by about 8 wave-numbers.

The fourth group of lines, namely 287, 299 and 364, appear as a doublet with frequency shifts of 343 and 380 in the molten state and a single diffuse band with the centre at 355 in the aqueous solutions. Its presence could not be detected in alcoholic solutions due perhaps to the strong halation following the Rayleigh line.

Of the lines in the fifth group in the solid 124 and 199 completely disappear in the liquid and the solutions, while 254 appears but weakly only in the molten state.

Besides these lines, the water band is present in the aqueous solutions and is prominent when they are dilute. The triple structure of the band is clearly seen and no apparent change in the relative intensities of components is observed. The acid has also practically no influence on the lines of methyl alcohol.

---

* A study of the polarisation of the acid shows that this line is composed by two different lines and will be reported upon in due course.

4. *Dissociation of Selenious Acid.*

The molecular conductivity of dilute aqueous solutions of Selenious acid[3] has been determined by Ostwald who finds that even at a dilution of 1024 litres the conductivity is only about 60% of that of a monobasic acid showing thereby, that it is a very weak acid. He has concluded that it is practically a monobasic acid which assumes the formula $(HO.SeO_2).H$. Therefore, in the aqueous solutions of all concentrations that are investigated by us, we can expect the presence of only the undissociated H_2SeO_3 molecules and $HSeO_3'$ ions formed during the first stage of ionisation.

The Raman specrta of aqueous solutions of concentrations varying from 100% to 7·5% by weight are identical and consist of two prominent lines at about 895 and 695 and a weak, diffuse band at 355. There is sensibly no variation also in the relative intensities of these three lines. These facts point out that the proportion of the molecular species giving rise to them remains practically the same at all concentrations.

Of these three lines, it is significant that the line 895 appears more or less in the same position in the solid, and aqueous and alcoholic solutions. Small changes in the frequency shift of this line depending upon the solvent and the state of dilution are only of an order which could be attributed to the influence of the solvent molecules. For purposes of comparison the frequency shifts of the acid and the salts are collected together in Table IV. The line which corresponds to the symmetrical expansion and contraction of $HSeO_3'$ ion appears at 862 in sodium biselenite.

The proximity of the frequency shift 895 in the acid to the symmetrical line in the biselenite suggests that the former is to be attributed to the $HSeO_3'$ ions in the acid.

On the other hand, the second intense line, 690 in the aqueous solution does not appear in the alcoholic solution, and is rendered weak in the solid; instead, another line is present at about 598 in the latter cases. These two lines presumably belong to two different forms of the undissociated molecule and are discussed fully in a later section.

The spectrum of sodium selenite consists of two lines of medium intensity with frequency shifts of 806 and 862 and two other feeble lines, as is to be expected if we assume a pyramidal model for the SeO_3 radical. The absence of any line at 806 at a concentration of 7·5% clearly indicates that the second stage of ionisation does not begin even at this stage.

---

[3] Landolt and Börnstein Tabellen. 1112.

TABLE IV.

$NaHSeO_3$	Na_2SeO_3	H_2SeO_3 (molten)	H_2SeO_4 10% Aq.
		238 (1)	
335 (1 dif.)		343 (4)	327 (3 *br*)
	375 (1)	380 (3)	390 (3 *br*)
603 (1)	598 (0)	545 (1)	
	734 (1)	690 (10 *br*)	737 (3 *br*)
	806 (5)		846 (1)
862 (5)	862 (5)		866 (10)
		892 (10 *br*)	910 (0)
			929 (1)

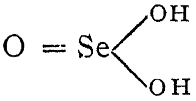
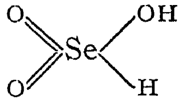
TABLE V.

$NaHSO_3$	Na_2SO_3	H_2SO_3	H_2SO_4 (incomplete)
242 (1)			
320 (1)			
420 (1)	471 (1)		521
565 (3)	602 (1)	569	574
826 (1)			
985 (2)	984 (4)		985
1009 (2)		1047	1047
		1142 (*str*)	
		1199	

The general conclusion, therefore, regarding ionisation of the acid is that the dissociation of $H_2SeO_3 \rightarrow H^\circ + HSeO_3'$ starts from the solid and the degree of dissociation remains practically constant at the concentrations employed. In agreement with the conductivity measurements, no further ionisation of $HSeO_3'$ is evident even in dilute solutions.

It has been reported recently that selenic acid[4] behaves in the Raman effect in the same manner as its analogue, sulphuric acid. But the selenious acid shows marked differences from sulphurous acid. In Table V the Raman frequencies of sulphurous acid and its salts are reproduced from a paper by Fadda.[5] Unlike selenious acid, there is no common likeness between the spectrum of this acid and those of Sodium sulphite and bisulphite. The lines 569 and 1047 are similar to those attributed to HSO_4' ions in sulphuric acid and are, therefore, due to the oxidation of a part of sulphurous acid to sulphuric acid. As can be seen from Table V there is no such common lines between selenic and selenious acids and hence shows that the latter does not undergo oxidation so easily as sulphurous acid. The presence of the strong line at 1142 in sulphurous acid which is characteristic of SO_2 gas,[6] confirms that further, most of the gas exists in a state of solution with water and only a small percentage of it is probably present as H_2SO_3 molecules. The line 1199 has been assigned to HSO_3' ions. Thus selenions acid seems to be more stable than its analogue sulphurous acid.

5. *Constitution of Selenious Acid.*

According to chemical evidence, the two possible forms in which selenious acid could exist are the symmetrical form  $O = Se(OH)_2$ or the unsymmetrical form  $O_2Se(OH)H$. In the former, selenium is quadrivalent and both the hydrogen atoms belong to the hydroxyl groups. In the latter, selenium is hexavalent and the acid is the pseudo-acid in which changes in constitution take place to restore it to the first type before any physical or chemical reaction starts with it. From a study of the heat of solution of this acid in different solvents Karve[7] concludes that it is an associated pseudo-acid in the pure condition and the aqueous solution contains a small percentage of the hydrate of the true acid. However, measurements of conductivity, hydrogen ion concentration, heat of solution and other physico-chemical properties do not always lead to conclusive results[8] regarding the true nature of the acid.

---

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

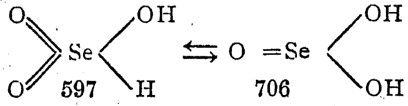
[5] Fadda, *Nuovo Cimento,* 1932, **9**, 168.

[6] Bhagavantam, S., *Ind. Jour. Phys.*, 1931, **6**, 319.

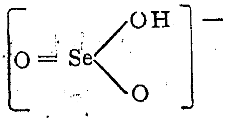
[7] Karve, D. D., *Jour. Ind. Chem. Soc.*, 1925, 2, 128.

[8] Stewart, A. W., *Some Physico-Chemical Themes,* Longmans, 1922.

From the point of view of the Raman effect it is evident that the two forms of the acid given above should yield their own lines of entirely different frequencies. As has been pointed out before, one of the striking features in the spectra of the acid in the different states of existence is the remarkable change in the intensity of the two lines 706 and 597 of the solid as it passes to solution in water. These changes in intensity could be easily understood on the postulate that the two forms of the acid are in a state of dynamic equilibrium as follows :—



The line with a frequency shift of 597 is characteristic of the unsymmetrical type and 706 of the symmetrical type. The former is more predominant than the latter in the solid and hence the increased intensity of the line 597. The existence of the line 706, in the crystalline acid shows that the latter type is also present in it. As is to be expected, solution of the acid in methyl alcohol contains only the unsymmetrical form and gives the intense line at about 589. In the aqueous solution the reverse process sets in and almost the whole of the acid assumes the symmetrical structure. This contributes to the increased intensity of the line 706. In the molten state when the acid is in solution with its water of crystallisation, a weak line is present at 567 and indicates the persistence of the unsymmetrical form under that condition.

According to the theory of pseudo-acids the first ionisation product of both the types of molecules is identical and the biselenite ion has a structure . Hence irrespective of the molecular species existing in the solid and the aqueous and the alcoholic solutions, a certain percentage of $HSeO_3'$ ions is formed during the first stage of dissociation and this accounts for the appearance of the line of frequency shift of 895 more or less in the same position in all states.

Thus, the solid or the soultions present a complicated system consisting of two or three molecular species and it is difficult to assign the low frequencies that are observed to any one of them. But in comparison with the Raman spectra of iodic acid[9] or nitric acid, it may be suggested that the two low frequencies at 343 and 380 in the molten liquid which appear as a single diffuse line at 355 in more dilute solutions

---

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

belong to the vibrations corresponding to the second parallel vibration of the molecules of the AX_3 type. Of these 343 coincides fairly well with the low frequency at 335 in the sodium biselenite and is due to $HSeO_3'$ ions. The corresponding line of the SeO_3 radical appears at 375 in the sodium selenite solution. The other frequency 380 may, therefore, belong to the symmetrical form of H_2SeO_3 molecules. As has been discussed before, these two frequencies of the solution are replaced by three sharp lines 287, 299 and 364 in the solid. There is one more line at about 524 which is of medium intensity in the solid and which is present weakly in the aqueous solutions of the acid. This line is also to be attributed to one of the normal modes of vibration of the H_2SeO_3 molecule. The corresponding line of $HSeO_3'$ ion appears diffuse at 603 in the biselenite and of SeO_3 radical appears at 734 in the selenite of sodium.

6. *Low Frequency Oscillations.*

Besides the lines discussed above, there are three lines at 124, 199 and 254 in the solid. Their antistokes are clearly seen in the excitations by the 4047 radiations of the mercury arc. The first two completely vanish on going to solution and the third appears weakly only in the molten state. In the case of iodic acid and iodates,[10] the author has observed similar lines and pointed out some difficulties in assigning them to lattice oscillations as put forward by Gross and Vuks[11] to explain the lines discovered by them in the crystals of diphenyl ether, naphthalene, dibromobenzene and benzene. Bhagavantam[12] has suggested that in the latter cases the lines are due to the incomplete rotations of molecules as pictured by Pauling. Recently Sirkar[13] has investigated the problem more thoroughly and finds that these lines owe their origin to intermolecular vibrations in groups of molecules which persist in some cases in solution and that they are affected by changes of temperature. In view of these discussions, it is probable that the line 254 of the crystals of selenious acid which appears feebly in the liquid state is due to polymerised groups of molecules and the lines 124 and 199 are due to hindered rotation of individual molecules. But a more definite conclusion can be arrived at only by studying the effect of change of temperature on these lines and work in this direction is in progress.

7. *Change of State and Raman Effect.*

The changes that take place in the main Raman lines of selenious acid as it passes from the solid to the molten state are illustrated in the accompanying

---

[10] Venkateswaran, C. S., *loc. cit.*

[11] Gross and Vuks, *Nature,* 1935, 135, 100, 431, 998; *Jour. de Phys.,* 1935, **6**, 457.

[12] Bhagavantam, S., *Proc. Ind. Acad. Sci.,* A, 1935, 2, 63.

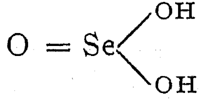
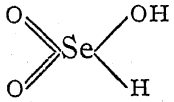
[13] Sirkar, S. C., *Ind. Jour. Phys.,* 1936, **10**, 109.

plate. Just as in the case of selenic acid[14] the sharp lines of the solid are replaced by broad and intense bands which tend to become narrower in the less concentrated solutions. The extraordinary breadth of these bands is partly explained by supposing that they consist of several components which appear as single, sharp lines in the crystals. But, in general, this feature is characteristic of associated liquids like sulphuric, iodic, formic and acetic acids and therefore, is to be attributed to association of molecules in them. In nitric acid in which there is no association the lines are comparatively sharp. The lines also suffer changes in frequency which is characteristic of hetro-polar compounds. In both selenic and selenious acids this change is pronounced in the lower degenerate vibrations.

In conclusion, the author wishes to thank Professor Sir C. V. Raman for his keen interest in the work.

Summary.

The Raman spectra of selenious acid as crystals and as aqueous and alcoholic solutions of varying concentrations as well as those sodium biselenite and sodium selenite are investigated. The solid has yielded a spectrum rich in sharp and intense lines, of the following frequencies :—124, 199, 254, 287, 299, 364, 524, 597, 706, 862, 889, 909 and 940 cm.$^{-1}$ The lines broaden out and undergo variations both in frequency shift and intensity.

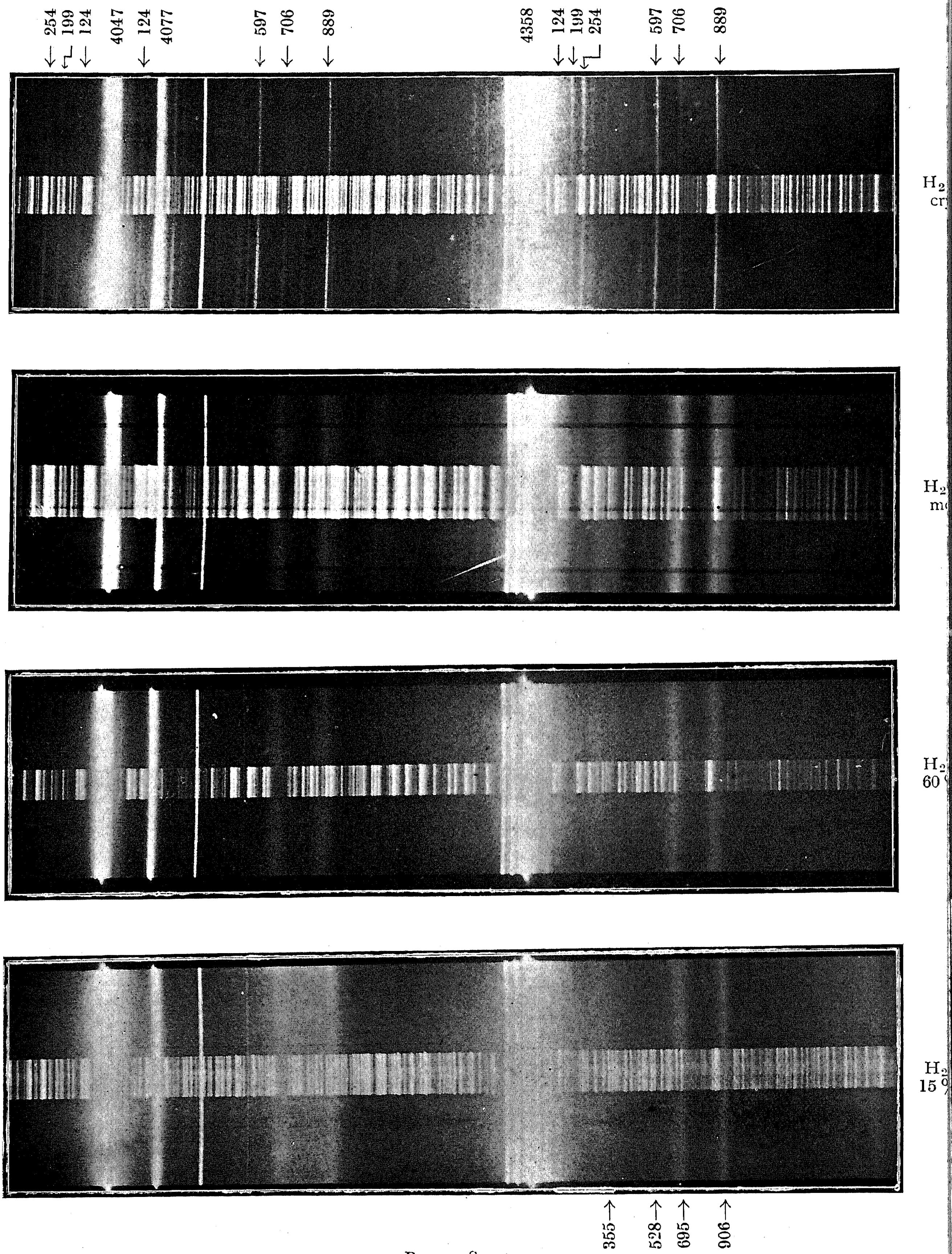
The changes in relative intensities of the two lines, 706 and 597, are particularly remarkable and are explained by postulating two types of molecules namely the symmetrical form  $\mathrm{O = Se}\begin{smallmatrix} \diagup \mathrm{OH} \\ \diagdown \mathrm{OH} \end{smallmatrix}$ and the unsymmetrical form  in dynamic equilibrium in the acid. In the solid and in the solution in methyl alcohol the latter is the more predominent type and in the aqueous solution almost the whole of the acid is converted to the former type. Thus the Raman effect data are made use of for the first time to explain the pseudo or the true nature of the acid.

The spectra of aqueous solutions of different concentrations indicate that the dissociation of the acid is weak and that, the proportion of molecules dissociated to $HSeO_3'$ ions remains practically constant throughout. The line 895 is assigned to the $HSeO_3'$ ions. The results are compared to those of its analogue, sulphurous acid. The other lines in the spectrum are attributed to vibrations of definite molecular species by comparing them to the lines in the sodium salts of the acid.

---

[14] Venkateswaran, C. S., *loc cit.*

C. S. Venkateswaran. *Proc. Ind. Acad. Sci., A, vol. III, Pl. XXVI.*



Raman Spectra.