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The Raman Spectrum of Sulphuric Acid

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A study was made of the Raman spectrum of sulphuric acid at concentrations varying every five percent from 100 to 5 percent by volume. A dispersion of 10A/mm at 4200A and 15A/mm at 4500A was used. Eight lines were found, which varied gradually in frequency, width, and intensity with changing concentration. Their frequency ranges are

408–432, 56f–596, 913–895, 970–973, 980–983, 1031–1051, 1142–1174, 1216–1236, 1352–1332. A gradual change in frequency with concentration was found for a number of the lines. The measurements were checked with a microphotometer.

A NUMBER of investigators have studied the Raman spectrum of sulphuric acid at varying concentrations. This substance is of particular interest because of the presence of molecules and two types of ions. In addition to giving data on the molecular structure, Raman spectra give information regarding the relative abundance of the ions. Nisi¹ found that the lines change in intensity and width with increasing dilution. Ramakrishna Rao² and Woodward and Horner³ reported a frequency shift for some of the lines. The latter found that this shift could be interpreted on the basis of components of slightly different frequency which appeared and disappeared at different concentrations.

In a preliminary report⁴ the writers found evidence of a gradual shift rather than components. It was not possible to decide fully whether components existed without a more exhaustive study. Consequently, the Raman spectrum was photographed every five percent from 100 to 5 percent by volume. The conventional set-up with mer-

cury excitation was used. A prism spectrograph was used with a dispersion of 10 A/mm at 4200A and 15 A/mm at 4500A. Lines excited by both 4047A and 4358A were measured as a check on the frequencies. The temperature was kept fairly constant during exposures which varied up to seventy-two hours. Among the difficulties encountered was the continuous background which was especially troublesome for 100 percent acid (F.P. 10.45°C). The broad water band at low concentrations masked some of the lines excited by 4047A. The plates were measured on a comparator and the frequencies calculated from an iron comparison spectrum. For the sharp lines they are accurate to about 3 cm⁻¹; for the broad ones to about 5 cm⁻¹. These frequencies with the widths and intensities are given in Table I. Measurements made with KHSO₄ and Na₂SO₄ solutions are given in Table II.

It will be seen from Table I that all of the eight lines have varying characteristics at different concentrations. Line 1 is present everywhere except at very low concentrations. It could not be measured at 100 percent on account of the strong continuous background. The intensity of the nearby mercury lines made the measurements

¹ Nisi, Jap. J. Phys. 5, 119 (1929).

² Ramakrishna Rao, Ind. J. Phys. 8, 123 (1933).

³ Woodward and Horner, Proc. Roy. Soc. A144, 129 (1934).

⁴ Bell and Jeppesen, J. Chem. Phys. 2, 711 (1934).

TABLE I.

Vol. %	Line	1	2	3	4	5	6	7	8	Mole %
100		562 (m)	911 913 30 6				(1142)			100
95	409 (m)	561 910 971	972 1038 1151	1038 1153					(f)	86
90	408 (f)	565 (m)	910 970	1038 1153					(f)	75
85	412 (f)	570 (m)	910 970	1038 1153					(f)	65
80	417 (f)	577 (f)	907 904	1035 1032					(f)	58
75	418 (f)	579 (f)	905 906	1034 1032					(f)	51
70	424 (f)	582 (f)	903 901	1034 1031					(f)	45
65	423 (f)	583 (f)	897 900	1035 1031					(f)	39
60	425 (f)	586 (f)	899 900	1036 1036					(f)	34
55	426 (f)	585 (f)	897 900	1036 1036					(f)	29

Vol. %	Line	1	2	3	4	5	6	7	8	Mole %
50	426 (f)	588 (w)	897 983	982 1038						25
45	425 (f)	588 (w)	897 983	981 1037						22
40	427 (f)	589 (w)	897 982	982 1039						19
35	427 (f)	590 (w)	896 980	982 1042						16
30	427 (f)	593 (w)	896 980	982 1045						13
25	425 (f)	594 (w)	897 980	982 1048						10
20	429 (f)	592 (w)	897 981	981 1048						7.8
15	432 (f)	592 (w)	895 981	983 1050						6.0
10	432 (f)	592 (w)	895 981	983 1051						3.6
5										1.8

(f) too faint to be measured on comparator
(w) masked by water band
(m) masked by mercury line
() uncertain

The columns refer to the several lines observed. For a given concentration the first number is the $\Delta\bar{\nu}$ from 22,938 cm^{-1} (4358A), the second the $\Delta\bar{\nu}$ from 24,705 cm^{-1} (4047A), the third the width of the line in cm^{-1} , and the fourth the intensity.

at low concentrations uncertain. This line is broad and of constant intensity at all concentrations. It seems to increase in frequency as is shown in Fig. 1. Line 2 is similar to line 1. It has the same width and is a little more intense. It appears at all concentrations from 100 to 10 percent and gradually increases in frequency. The excitation from 4047 coincides with the 4142 mercury line at high concentrations, but is easily separated at low concentrations. The similarity of lines 1 and 2 may mean that they originate from the same scatterer.

Line 3 is the most intense line at 100 percent and practically disappears for very dilute solutions. It broadens noticeably and decreases in frequency for low concentrations. Its great intensity at 100 percent seems to indicate a con-

nection with the molecule. Line 4 appears first at about 55 percent and increases in intensity with dilution. The frequency remains constant as far as can be determined, and the line is uniformly sharp wherever it appears. Because its frequency checks with the strongest line observed in sulphate solutions (Table II), it has been ascribed to the SO_4 ion. This would indicate the presence of a large number of SO_4 ions from 35 to 5 percent. From 95 to 85 percent a weak 971 cm^{-1}

TABLE II.

	Mole %	$\bar{\nu}$	$\Delta\bar{\nu}$
KHSO_4	2.2	21,955	983 (4)
		21,890	1048 (5)
Na_2SO_4	0.4	21,958	980 (5)
		23,724	981 (4)

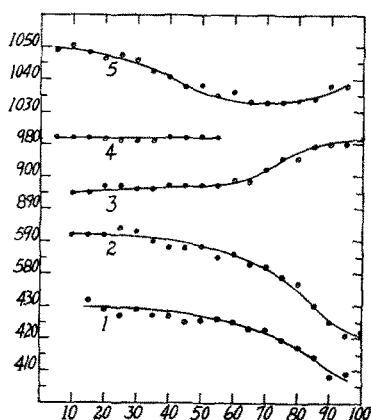


FIG. 1. Average frequencies of the five most intense lines plotted against the concentration in volume percent.

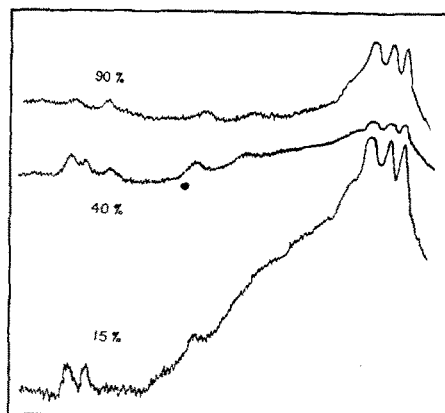


FIG. 2. Reproduction of microphotometer curves of lines excited by 4358Å.

line is found. It is entirely absent at low concentrations. It should not be confused with the 981 cm^{-1} line. The strong continuous background may mask it at 100 percent. Line 5 does not appear at 100 percent, but shows up faintly in pure acid which has been exposed to the air for only a few hours. Since this is in agreement with the strongest line found in acid sulphate solutions (Table II), it has been ascribed to the HSO_4^- ion. The intensity variation shows that this ion is present in solutions containing only a trace of water and that it is present in great abundance from 45 to 5 percent. Its frequency seems to decrease slightly and then increase. Sufficient data are not available to determine whether this frequency shift is also characteristic of the 1048 cm^{-1} acid sulphate line.

Line 6 is never strong but appears at practically all concentrations. A shift of 1146 cm^{-1} has been reported⁵ for SO_2 solutions. Line 7 was not found at 100 percent, but at intermediate concentrations it is slightly more intense than line 6. Woodward and Horner found evidence for this line in their microphotometer curves. Line 8 appears very faint at a number of concentrations. It is in approximate agreement with the 1340 cm^{-1} SO_2 line.⁵ The frequency shift of lines 6, 7 and 8 is open to question on account of the difficulty in measuring such weak lines. They could be measured best in the region excited by 4047

because of the absence of background. The 3450 cm^{-1} water band first appears at 80 percent. It broadens and increases in intensity with dilution. Siva Rao⁶ has found a gradual decrease in frequency for this band, going from 3468 cm^{-1} at 32 percent to 3424 cm^{-1} for pure water. A careful search failed to show any lines corresponding to S—H or O—H bonds in sulphuric acid.

If each line consists of components whose intensities depend upon the concentration there should be a particular concentration favorable to the simultaneous appearance of two components. Photographs taken every 5 percent have failed to reveal this. If they do exist their frequency differences must be much less than that previously reported. On the other hand a gradual shift is indicated for some of the lines. This is shown in Fig. 1. In most cases the change is most rapid around 85 percent.

Microphotometer measurements were made over the range studied. Three representative curves are reproduced in Fig. 2. The symmetrical shape of all the lines makes the existence of any components doubtful. A study of all the microphotometer data seems to verify the frequency, width and intensity variations reported in Table I.

The writers wish to thank the Physics Department of Johns Hopkins University for the use of their microphotometer.

⁵ Bhagavantam, Ind. J. Phys. 5, 59 (1930).

⁶ Siva Rao, Ind. J. Phys. 9, 195 (1934).