JUNE 15, 1931 PHYSICAL REVIEW VOLUME 37

RAMAN SPECTRA OF SULPHURIC ACID

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(Received May 11, 1931)

Abstract

Concentrated H_2SO_4 gives a series of Raman lines which, with the exception of the 4566A line, decrease in number and intensity with a decrease in concentration and finally disappear. At the point at which the above lines vanish, a broad line (4817A) appears and persists in dilute solutions. At low concentrations the water bands are present. The 4566A line is present at all concentations of acid and increases in intensity with a decrease in concentration, but is missing in pure water. A line with the same wave-length (within experimental error) and intensity variation is found in HNO_3, and it is suggested that the two lines have the same origin.

RAMAN spectra have made possible a new approach to the study of conditions in acids at various dilutions. Rao[1] found that the Raman lines obtained from HNO_3 could be classified into the three following groups according to their behavior as the acid was diluted: (1) those due to the HNO_3 molecule, (2) those due to the NO_3^- ion, and (3) those due to the water molecule. The lines of the first group decrease in intensity as the concentration is decreased and finally disappear. The lines in the second group increase in intensity as the concentration is decreased, reaching a maximum at the concentration when the lines of the first group vanish, and then these lines also decrease in intensity. The lines of the third group appear as bands which first appear faintly as the acid is somewhat diluted and gradually increase in intensity and broaden as the concentration is decreased. The purpose of this paper is to present similar data obtained from sulphuric acid at various dilutions. A preliminary account of data has previously been reported in a letter to Nature.[2]

The method used to obtain spectrum was similar to the general method described by R. W. Wood,[3]—using a mercury arc. Most of the photographs were taken with a prism spectrometer, but plates were also obtained with a plane grating on the spectrometer table in place of the prism. The latter arrangement gave greater dispersion, but the intensity was, indeed, greatly reduced.[4] Definite traces of lines and bands were found at all concentrations. With the prism, most of the lines could be obtained with an exposure of three minutes and the strongest could be detected on plates of a minute exposure. The lines in Table I are all taken from plates with 30 minute exposure,—

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[1] Rao, Proc. Roy. Soc. **A127,** 279 (1930).

[2] Bell and Fredrickson, Nature **125,** 895 (1930).

[3] R. W. Wood, Phil. Mag. **6,** 729 (1928).

[4] Attempts were made to obtain Raman spectra with a small concave grating of 120 cm focus, but without success.

with experimental conditions exactly the same throughout. A fifteen hour exposure with the grating gave the same intensity as the thirty minute prism exposure and those lines are listed in Table II. The concentrations are measured in mol percent. That is, 50 percent concentration is one H_2SO_4 molecule to one H_2O molecule; 100 percent is the purest acid available, commercial 96 percent; and 0 percent is pure distilled water. The wave-lengths are accurate to 3A. The numbers in parentheses are eye estimates of the intensity of the lines.

TABLE I. *Raman spectrum of H_2SO_4 (Prism).*

Concentration (percent)	Wave-length in Angstroms						
100			4585 (1)	4566 (1)	4542 (4)	4470 (3)	4438 (3)
90				4566 (1)	4542 (3)	4470 (3)	4438 (3)
80				4566 (2)	4542 (3)	4470 (3)	4438 (3)
70				4566 (2)	4542 (2)	4470 (2)	4438 (2)
60				4566 (2)	4542 (2)	4470 (2)	4438 (2)
50				4566 (3)	4542 (1)	4470 (2)	4438 (2)
40	4817			4566 (3)	4542 (1)	4470 (2)	4438 (2)
30	4817			4566 (3)			
20	4817	4750 to 4700		4566 (3)			
10	4817	4750 to 4700		4566 (2)			
0		4750 to 4700					
100	4276 (0)	4252 (0)	4224 (3)	4203 (4)	4171 (0)	4142 (2)	
90			4224 (3)	4203 (3)	4171 (0)		
80			4224 (3)	4203 (3)			
70			4224 (2)	4203 (2)			
60			4224 (2)	4203 (1)			
50			4224 (1)	4203 (1)			
40			4224 (1)	4203 (0)			
30							
20			4225 to 4175				
10			4225 to 4175				
0			4225 to 4175				

Notes. 4817 was a broad line or band at all times.
4566 became broad at low concentrations.
4750 to 4700 and 4225 to 4175, water bands, became sharper and less intense as concentration increased.

TABLE II. *Raman spectrum of H_2SO_4 (Grating).*

Concentration (percent)	Wave-length in Angstroms							
100	4585 (1)	4566 (1)	4540 (4)	4470 (3)	4440 (2)	4279 (0)	4225 (1)	4203 (2)
80		4566 (2)	4540 (3)	4470 (3)	4440 (2)		4225 (1)	4203 (1)
60		4566 (3)	4540 (3)	4470 (3)	4440 (2)		4225 (0)	4203 (1)
40		4566 (4)	4540 (2)	4470 (3)	4440 (2)		4225 (0)	4203 (0)
30		4566 (3)	4540 (1)	4470 (1)	4440 (1)		4225 (0)	4203 (0)

From Table I we see that the lines found in concentrated H_2SO_4 persist as far down as 40 percent. The lines given for 100 percent agree with the results obtained by Ganesan and Venkateswaran[5] with concentrated H_2SO_4. The intensity of all lines except the 4566 line decreases in intensity with a decrease in the concentration. The 4566 line, however, increases in intensity to a maximum and then broadens and decreases in intensity. The two water bands are in approximate agreement with the measurements given by others. It is interesting, however, to note the decrease in breadth and the sharpness of these bands at their first appearance at high concentrations. The origin of the 4817 line or band is uncertain. It makes its appearance when the other lines disappear and is always broad. The 4470 line is the only one which seems to indicate a shift in wave-length as the concentration is decreased. On some of our plates there is a slight indication that this line has shifted slightly to the red.

The lines obtained with the grating, as listed in Table II, are similar to those in the preceding one. Here even the 30 percent concentration shows some of the H_2SO_4 molecule lines. The most striking thing about the grating plates is the change in intensity with concentration. The 4540 line decreases considerably in going from 100 to 40 percent, while the 4566 line increases correspondingly.

Comparing the above results with those reported by others we find two interesting facts. (1) Several experimenters[6] working with sulphates find in all cases lines at 4552A and 4214A which they attribute to the $SO_4^=$ ion. Our plates fail to reveal these lines, not even the plates of very long exposure time. (2) Rao[7] reports a line at 4567A which he finds at all concentrations of HNO_3. We also find a line at 4566A which appeared at all concentrations. Ganesan and Venkateswaran[8] give 21895 cm^{-1} as the measurement for the same H_2SO_4 line and 21893 cm^{-1} for the HNO_3 line. Both of these lines increase in intensity with a decrease in concentration. Neither line appears in pure distilled water. We are inclined to believe that this close agreement in wave-length and variation in intensity with concentration is not fortuitous, but rather an indication that the two lines may have the same origin—perhaps a hydrated hydrogen ion.

The experimental work described above was done in the Department of Physics at Syracuse University.

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[5] Ganesan and Venkateswaran, Ind. Jour. of Phys. **4**, 195 (1929).

[6] Mukherjee and Sen Gupta, Ind. Jour. of Phys. **3**, 503 (1929). Hollaender and Williams, Phys. Rev. **34**, 994 (1929).

[7] Rao, reference 1.

[8] Ganesan and Venkateswaran, reference 5.