FREQUENCY CHANGES IN THE RAMAN SPECTRUM
OF SULPHURIC ACID

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ABSTRACT. Changes in the frequency of the Raman lines of sulphuric acid with dilution are measured. The low-frequency bands 415 and 570 are shifted away from the Rayleigh line, and the 913-line shifts towards it, with increasing dilution The 1040 first decreases in Raman frequency with dilution, and, on further dilution, its frequency is increased, while the 984 line remains unchanged In solution of acid sulphate, the 913, 1040 and 984 have less frequency as compared with equivalent solution of sulphuric acid. Besides, all the lines are diffuse and broad in intermediate concentrations.

The changes in the low-frequency bands are attributed to the changes in the relative abundance of H SO₄, HSO₄ and SO₄ radicals in solution with change in concentration. The behaviour of 913 is attributed to the relative abundance of H₂SO₄ and HSO₄ radicals, each of which contributes a component to this band. The 984- and 1040-lines owe their behaviour to the combined effects of (1) ions surrounding each of SO₄ or HSO₄ ions and (2) hydration. The lower frequency in the acid sulphate solution as compared to the equivalent acid solution, is attributed to the predominence of hydration over the effect of surrounding ions, due to the smaller percentage of H ions in the former.

INTRODUCTION

In a previous communication,[1] the author reported investigations on the progressive dissociation of sulphuric acid with dilution, from a study of the intensity changes in the Raman lines of this substance with change in concentration. Equally interesting are the changes in the Raman frequencies of this substance with dilution.

A characteristic feature of sulphuric acid is that all its Raman lines are broad and diffuse. This is the reason why the values for the frequencies of the lines and their changes on dilution, given by various authors differ to a large extent. Also, the continuous spectrum which is superposed on the Raman lines adds to the difficulties in locating the maxima and extents of the bands. Nisi[2] reported that the Raman lines suffer a general shift towards higher frequency on dilution and explained the result as due to the hydration of the molecules. Specchia[3] observed a similar result. Ramakrishna Rao,[4] while agreeing that the low-

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frequency bands with maxima 385-450 and 543-608 shift away from the Rayleigh line on dilution, expressed doubt as regards the increase in the frequencies of the 913-860 and 1040-1037 lines since they are of the same order of magnitude as the experimental error. Woodward and Horner [5] stated that all the bands, except the 910-860, are shifted towards higher Raman frequency and their observations are in conformity with those of Bell and Jeppesen.[6] On the other hand, Bell and Fredricson,[7] working with a grating, observed no shifts except in the case of 543-608. But, none of the above authors explained these shifts. The present work is an attempt in this direction.

<h3 align="center">EXPERIMENTAL</h3>

To remove the intense continuous spectrum that is present in the Raman spectra of solutions of sulphuric acid, the acid is treated with a few drops of pure nitric acid and heated to about 200°C for about half an hour, following the suggestion made by Medard.[8] With the acid treated like this, clear spectra are obtained. In order to facilitate clear observation of the shifts, the spectra are taken using a Hartman diaphram. The experimental arrangement is the same as described in the previous communication.[1] Since the Raman lines are broad and diffuse, it is difficult to locate their maxima by a micrometer. Therefore, microphotometric curves are taken for the spectra and the frequencies of the maxima measured by using the Hartman dispersion formula. The values of the frequencies of the Raman lines and their widths at various concentrations are given in the following table.

<div align="center">TABLE GIVING THE FREQUENCIES OF THE RAMAN LINES IN SOLUTIONS OF SULPHURIC ACID, ACID-SULPHATE AND SULPHATE</div>

Concentration in gm. moles.	A			B			C			D			E
	Extent	Max	Width	Extent	Max	Width	Extent	Max	Width	Extent	Max	Width	Max
16.5	390—450	410 / 385	69	488—600	545	112	884—937	913	53	1005—1059	1040	54	
14.5	369—482	400	113	525—625	552	100	871—937	910	66	994 1066	1036	72	
12.5	369—404	408	125	525—620	570	95	852—937	905	85	998—1091	1030	93	984
10.5	369—478	408	109	525 620	570	95	862—926	890	64	963—1080	1030	117	984
7.5	380—467	415	87	536—620	578	95	862-930	887	68	1001—1080	1035	79	984
1.5	380—467	415	87	536—620	578	95	858—879	866	21	1001—1055	1039	54	984
3.0 KHSO₄	380—467	415	87	536—620	578	95	858—879	866	21	1001—1055	1039	54	984
3.0 (NH₄)₂ SO₄	373—452	415	79	536—620	578	95	858—879	860	21	1001—1055	1037	54	980
3.0	408—462	450	54	586—640	608	54	...	...	...	...	...	...	980

In the above table, the first column gives the concentration in gram. moles of the acid in 1000 c.c. of the solution. Each of the other columns, allotted for each of the lines, is subdivided into three, the first division giving the extent of the band, the second the Raman frequency of the maximum and the third the width of the band.

RESULTS AND THEIR EXPLANATION

For the sake of convenience, the Raman lines are lettered from A to E, A and B representing the low-frequency bands 385-450 and 543-608 C, D and E correspond to 913-860, 984-980 and 1040-1039, respectively. The other bands, *viz.*, 1171 and 1365, are very diffuse and feeble and disappear very quickly on dilution, and hence no attempt is made to measure their changes in frequency with dilution.

A.—Raman frequency 385-450

This band is found in the spectra taken with all the substances containing SO_4 radical, and hence is regarded as characteristic of it. It has a clear doublet structure at the highest concentration with maxima at 385 and 410. Bell and Jeppesen,[6] who have worked with 100% acid report that this structure is very prominent with the purest acid. In the spectra taken with dilute solutions of sulphuric acid and of acid sulphates there is only one diffuse band with its maximum at 415, and in sulphate solutions at 450. Therefore, it is concluded by Ramakrishna Rao[4] and Woodward and Horner[5] that 385-410, 415 and 450 are respectively characteristic of H_2SO_4, HSO_4 and SO_4 radical, respectively.

With increasing dilution the band is observed to be shifting away from the Rayleigh line and it is explained by Ramakrishna Rao[4] and Woodward and Horner[5] as due to the fact that with decreasing concentration, the H_2SO_4 molecules dissociate to HSO_4' and H^+ ions which brings about a diminution of intensity of the doublet on which is superposed the higher-frequency band excited by HSO_4 ions.

B:—Raman frequency 543-608

Like A, this band is also taken as characteristic of SO_4 radical for the same reason. In the pure acid, it has a single maximum at 543. With dilution, it behaves in a similar manner and just for the same reasons as in the case of A.

Bell and Jeppesen[6] objected to the above explanations Working with a large number of concentrations of the acid at intervals of 5%, they failed to observe at any concentration, a separation, of the two components due to HSO_4 and H_2SO_4 radicals. But, in view of the width and the closeness of the bands, no such separation can be expected. There can be only a shift in the resultant,

maximum and an increase in the width of the band as a result of the super-position of the components due to H_2SO_4 and HSO_4. This is what is actually observed.

C.—Raman frequency 913-860

This band is found to be very intense in the spectra taken with very concentrated solutions of the acid and as the concentration of the acid is diminished, its intensity diminishes more than in proportion to dilution. Hence it is attributed to the undissociated H_2SO_4 molecules.

But, in the spectra taken by the author, this band persists, though with much less intensity, even in dilute solutions and also in solutions of $KHSO_4$ but with a slight decrease in Raman frequency, a fact which has not been observed by any of the previous authors.

The band exhibits conspicuous changes in the frequency. Its width is 51 wave numbers in the highest concentration, and its maximum is at 913. But, as the dilution is increased, the maximum shifts towards lower-frequency and the higher-frequency portion of the band gets feebler. With increasing dilution, it becomes narrow with a width of 21 cm. which is the same as in $KHSO$; solution.

The behaviour of this band can be easily understood, if it is taken as composed of two components, a strong one with higher-frequency contributed by the H_2SO_4 molecules and feeble one contributed by HSO_4 ion. As the concentration of the acid decreases, the high-frequency component decreases in intensity, but, since the H_2SO_4 component is very strong compared to the HSO_4 component, the intensity of the band as a whole becomes feeble and gives the impression that the band is excited entirely by the H_2SO_4 molecules. In the intermediate dilutions, where both types of molecules are present, the band is naturally very broad and in the very low concentrations where the H_2SO_4 component is absent, the band is narrow and is shifted towards lower frequency.

D.—Raman frequency 1040

This band is taken to be characteristic of HSO_4 ion. It is very broad in solutions of moderate concentration of the acid, while in very concentrated solution it is less wide and in dilute solutions it is fairly sharp. Also, the maximum of the band shifts slightly but definitely towards lower frequency from high concentrations to moderate concentrations and shifts again from moderate concentration to dilute solutions. And in solution of acid sulphate it is of slightly lower frequency than in sulphuric acid of the same molecular concentration.

The larger diffuseness of this line in intermediate concentrations of the acid is in conformity with similar behaviour revealed in the course of investigations in this laboratory in general, by Raman frequencies of electrolytes, in the

intermediate concentrations, at which the band is usually most diffuse, and this is apparently due to the large ionic concentration of oppositely charged ions in the neighbourhood of each ion giving rise to the Raman frequency under consideration. In crystals, the line is the sharpest and of the highest frequency, when there is no water of hydration. In crystals, the disposition of the cation with respect to the axis of symmetry of the anion is the same for all the anions So, from solution to crystal there is only an increase in frequency without increase in diffuseness. But in intermediate concentrations of the acid solutions, where the number of cations surrounding each anion is the greatest, the relative disposition of the ionic field and the axis of symmetry of the anion is probably different for different ions, and hence, the Raman frequency may change slightly from ion to ion and this probably is the cause for diffuseness of the line in the intermediate concentrations.

As regards the change of Raman frequency, there are in general two causes giving rise to it (1) the surrounding ions and (2) water of hydration. The former have a tendency to increase the Raman frequency, while the latter diminishes it. In solutions of sulphuric acid, both these factors influence the Raman frequency, and the actual frequency at any concentration is due to the resultant of these two effects. It is difficult, however, to determine in the case of the changes exhibited by HSO_4 ions what part of the change is due to ionic influence and what part due to hydration, on account of the complications arising out of the superposition of the two effects.

The lower frequency of the band in acid-sulphate solutions, as compared with that of the acid of the same molecular concentration, seems to be due to the fact that there are less number of H^+ ions in the former. The hydrogen ions, in virtue of their lightness and smallness in size, can approach the negative ions much closer and hence can exert more influence than the heavy potassium ion can. Hence, in solutions of acid-sulphates, the effect of hydration is more predominent which, therefore, brings about a shift in the line towards lower frequency.

E.—Raman frequency 984

This line which is characteristic of SO_4'' ion, is very strong in solutions of sulphates and in dilute solutions of bisulphates. In solutions of sulphuric acid, it appears very feeble even in very dilute solutions. In high concentrations, the line appears very feeble and on it is superposed a part of the 1040-band. So, it is very difficult, either to locate the maximum in a microphotometric record or observe it by a micrometer. Therefore, nothing can be said regarding its changes in the frequency on diluting the acid. On comparing the line in the acid and acid-sulphate of the same molecular proportion, it is found that it is of slightly less frequency in acid-sulphates.

In solutions of the acid, probably the effect of ionic influence is just neutralised by that of hydration, so that there is no change in the frequency of this line. The lower frequency in solutions of acid-sulphates when compared with that of the acid is similar to that suffered by the HSO_4 ion probably due to the same reasons.

It is generally contended [9] that the greater is the chance for hydration of an ion in solution, (1) the larger the ionic charge, (2) the smaller the size in the case of cations (3) the larger the size in the case of anions. Also, oxygen is a better donor of electrons than hydrogen is an acceptor. Therefore, the anions in general are less hydrated than the cations.

But, in the present case, the HSO_4' ion is sufficiently large and contains many donor oxygens and hence is capable of being hydrated. The SO_4 ion contains 4 donor oxygens and doubly charged and hence is more easily hydrated than the HSO_4' ion. This is probably the reason why the shift of the E line from the acid to acid-sulphate is larger than the shift of the D line. The above view is supported by the fact that the crystals of sulphates are invariably hydrated with an odd number of H_2O molecules, e.g., $LiSO_4, 1H_2O$, $Na_2SO_4, 7H_2O$, $CuSO_4$, $5H_2O$, etc., shows that to the SO_4 ion is attached one molecule of water and it is supposed [9] to form a stable hexagonal ring of the constitution given below

$$O \diagdown \quad \nearrow O{\rightarrow}H \diagdown$$
$$\diagup S \diagdown \qquad \diagup O$$
$$O \diagup \quad \searrow O{\rightarrow}H \diagup$$
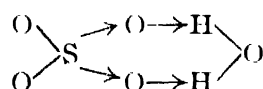
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