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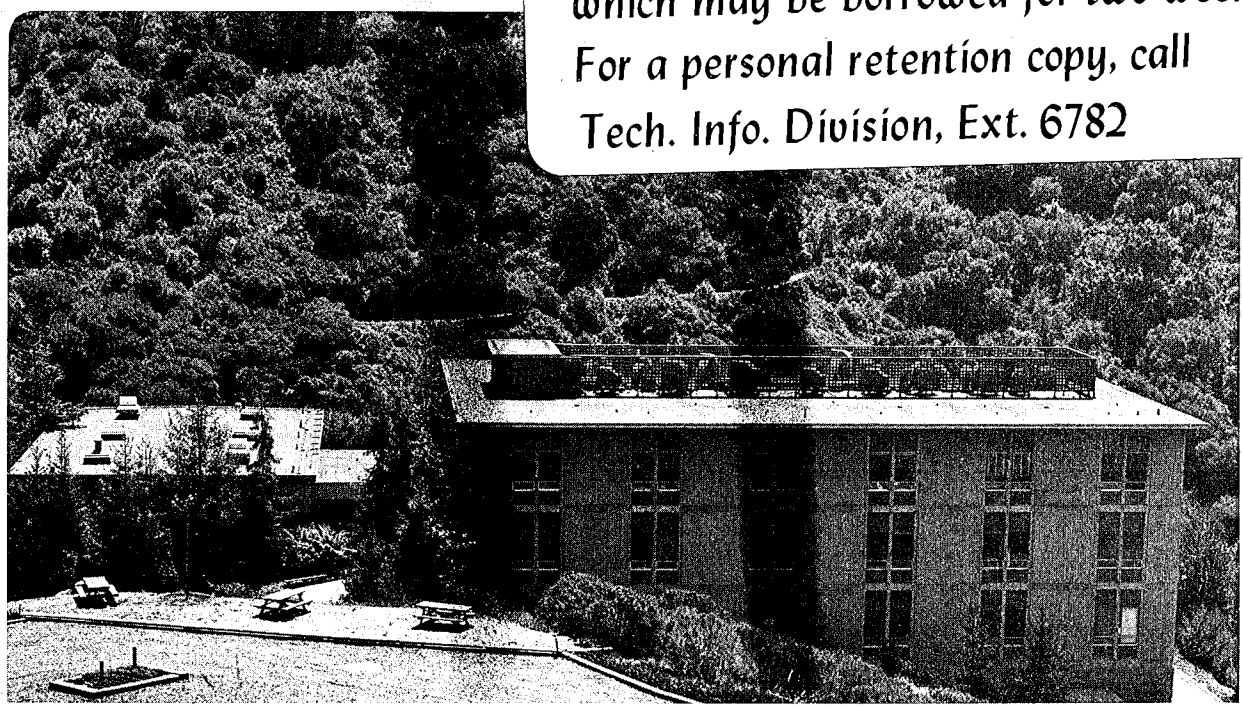
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THE EQUILIBRIUM CONSTANT FOR THE DIMERIZATION  
OF BISULFITE ION TO FORM  $S_2O_5^{2-}$

Robert E. Connick, Thomas M. Tam, and  
Eckart von Deuster

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THE EQUILIBRIUM CONSTANT FOR THE DIMERIZATION OF BISULFITE ION TO FORM  $S_2O_5^{2-}$ 

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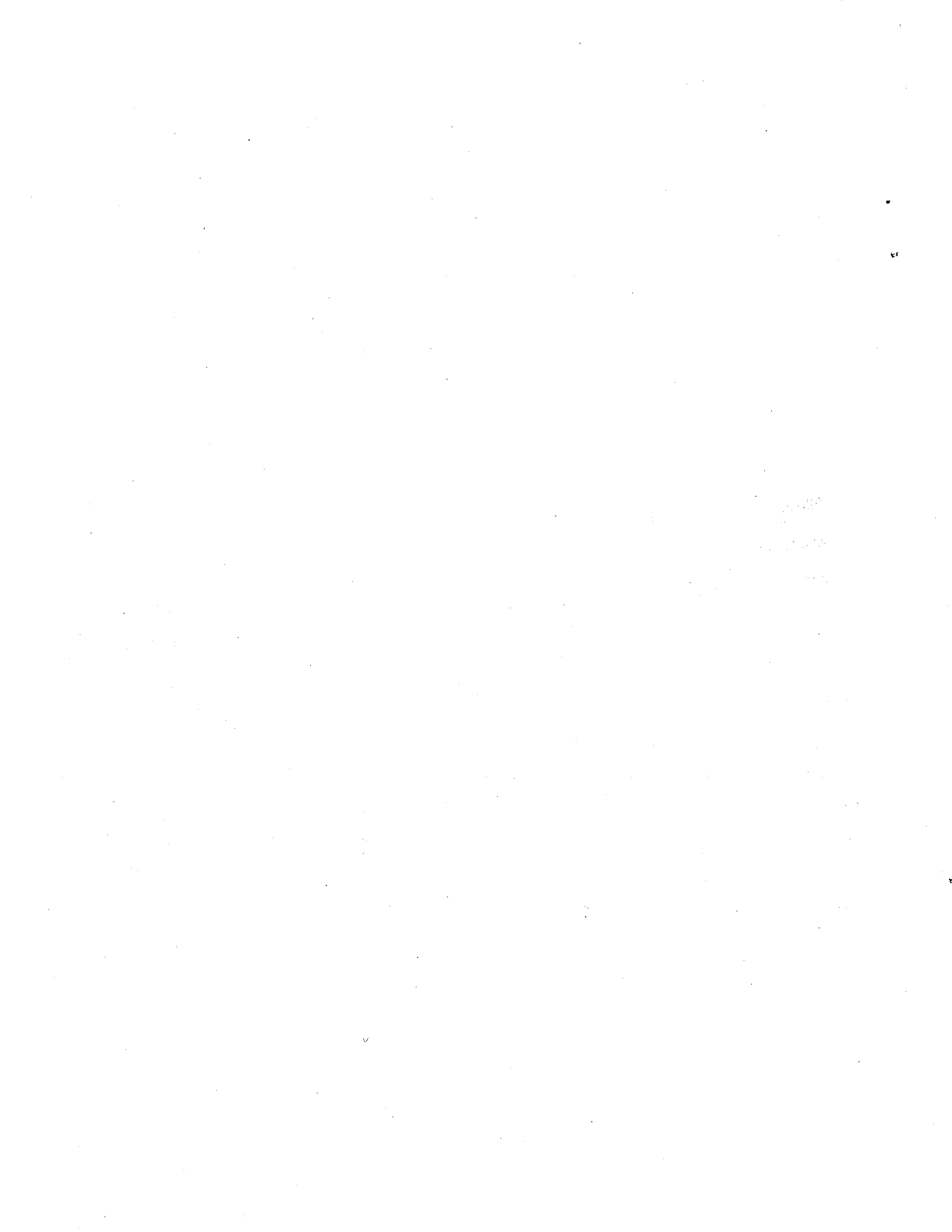
## ABSTRACT

At high concentrations in aqueous solution, bisulfite ion dimerizes to form the species  $S_2O_5^{2-}$ . The equilibrium quotient for the reaction:  $2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$  has been determined by combining Raman intensity measurements of  $HSO_3^-$  with ultraviolet absorption data on  $S_2O_5^{2-}$ . Unlike previous determinations, the method requires no assumption about constancy of the equilibrium quotient over the range of solutions measured, although it was necessary to assume a constant molar absorptivity in the UV for  $S_2O_5^{2-}$  and a constant molar Raman intensity for  $HSO_3^-$ . Earlier measurements reported in the literature, based only on UV measurements of  $S_2O_5^{2-}$  absorption and the assumption of constant equilibrium quotient and molar absorptivity, are shown to be seriously in error. Variations of the equilibrium quotient with ionic strength and temperature are reported. In addition to the well characterized form of bisulfite ion having the hydrogen attached to the sulfur, Raman evidence is reported for the presence of appreciable amounts of the isomer with the hydrogen bonded to one of the oxygens.

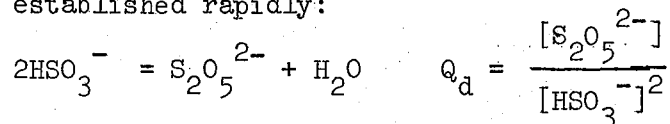
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In aqueous solutions of bisulfite ion, the following dimerization equilibrium is established rapidly:



Although several investigators<sup>(1,2,3)</sup> have attempted to measure  $Q_d$ , the results are far from concordant, as shown in Table 1, and an examination of the method used indicates that none of the values of  $Q_d$  is reliable.

All previous investigators measured the ultraviolet absorption of  $\text{S}_2\text{O}_5^{2-}$  in a region where  $\text{HSO}_3^-$  absorbs negligibly. The value of  $Q_d$  was obtained by a simultaneous fitting of the data with two parameters, assumed to be constant:  $Q_d$  and  $a_d$ , the molar absorptivity of  $\text{S}_2\text{O}_5^{2-}$ . To obtain reliable values for these parameters, it is necessary that an appreciable fraction of the total bisulfite be converted to the dimer at the highest concentration studied. A reexamination of Golding's<sup>(1)</sup> data shows no evidence of appreciable conversion. Arkhipova and Chistyakova<sup>(2)</sup> investigated such a small concentration range that their results could give no meaningful information on fraction conversion. Bourne et al.<sup>(3)</sup> made a careful study at constant ionic strength and applied corrections for the presence of  $\text{SO}_2$  and  $\text{SO}_3^{2-}$ . At their highest bisulfite concentration, 0.160 M, their interpretation of the data yielded five percent conversion to the disulfite dimer. But a five percent drift in  $Q_d$  could have equally well accounted for the data. Because  $Q_d$  is small, it is necessary to increase the bisulfite concentration to rather large values to produce appreciable conversion to the dimer. In doing so, the composition of the solution must be changed significantly, and consequently it is not safe to assume that  $Q_d$  will remain constant. Therefore in redetermining  $Q_d$  a method was sought which would not require the assumption of constant  $Q_d$  over the range of solution composition studied.

In the course of the study, information was obtained on the structure of bisulfite ion in solution. Evidence is presented that both isomeric forms of bisulfite, i.e., with the proton attached to the sulfur and with the proton attached to an oxygen, are present in solution in appreciable amounts.

Method: It would be desirable to have a physical measurement which would detect directly the concentration of bisulfite ion in the equilibrated solution. Unfortunately absorption spectra measurements will not do this, because  $S_2O_5^{2-}$  absorbs appreciably at all wavelengths where bisulfite ion absorbs, and there is no independent way of obtaining the molar absorptivity of  $S_2O_5^{2-}$ . Instead, the Raman emissivity of bisulfite ion was determined quantitatively from the intensity of the Raman line of the H-S stretch at  $2532\text{ cm}^{-1}$ . At the same time the ultraviolet absorption spectrum of the equilibrated solutions was also measured at 320 nm, a wavelength at which  $S_2O_5^{2-}$  absorbs strongly and the absorption of bisulfite ion is negligible. These data were then combined to give values of  $Q_d$ .

The Raman intensity,  $I$ , of the  $2532\text{ cm}^{-1}$  band should be directly proportional to the concentration of bisulfite ion<sup>(4)</sup>:

$$I = i[\text{HSO}_3^-] \quad (1)$$

with the proportionality constant  $i$ , the molar Raman intensity, unknown. The intensity divided by the total bisulfite, where,

$$[\Sigma \text{HSO}_3^-] = [\text{HSO}_3^-] + 2[\text{S}_2\text{O}_5^{2-}], \quad (2)$$

was plotted on a semi-log plot versus the total bisulfite concentration,  $[\Sigma \text{HSO}_3^-]$ .

The ultraviolet absorbance  $A$  is proportional to the concentration of  $S_2O_5^{2-}$

$$A = a_d \ell [\text{S}_2\text{O}_5^{2-}]$$

where  $l$  is the cell length. If the molar absorbance,  $a_d$ , were known, the concentration of  $S_2O_5^{2-}$  could be calculated, and by difference from the total S(IV), the concentration of  $HSO_3^-$  obtained, after correction for small amounts of  $SO_2$  and  $SO_3^{2-}$  present. Thus:

$$[HSO_3^-] = [\Sigma S(IV)] - [SO_2] - [SO_3^{2-}] - \frac{2A}{a_d l} \quad (3)$$

A plot of  $[HSO_3^-]$  divided by  $[\Sigma HSO_3^-]$  on a semi-log plot versus  $[\Sigma HSO_3^-]$  should yield the same curve as that of the Raman data except for a constant displacement on the vertical axis, corresponding to  $\log i$ . The shape of the curve of the ultraviolet data will depend on the value of  $a_d$ . By plotting a family of curves for different assumed values of  $a_d$  and comparing them with the shape of the curve from the Raman data, the one giving the best fit corresponds to the "correct" choice of  $a_d$ . Using this value, the composition and the value of  $Q_d$  can be calculated for any solution from ultraviolet absorbance data.

In the above treatment no assumption is made about the constancy of  $Q_d$ . It is necessary, however, to assume that  $a_d$  and  $i$  remain constant over the range of solution compositions studied. The assumption of constant molar absorbance in the ultraviolet region of the spectrum is commonly made and probably is justified. The assumption of constant  $i$  will be discussed in the section on results.

### Experimental

Sodium pyrosulfite (A.G.), sodium hydroxide (A.G.), sodium chloride (R.G.), and sodium perchlorate (R.G.) were used as supplied by Mallinckrodt Chemical and G. Frederick Smith Chemical Company. Sulfur dioxide (99.98% by weight) was obtained from Matheson Gas Products.



The sodium bisulfite stock solutions (5 M) were prepared either by adding sodium pyrosulfite to deoxygenated distilled water or by bubbling  $\text{SO}_2$  gas through a 5 M NaOH solution until the pH of the solution approached 5.5. In the former case, sufficient NaOH was added to convert 5 mole percent of the total bisulfite to sulfite ion to reduce the  $\text{SO}_2$  concentration and discharge the yellow color.<sup>(5)</sup> Solutions with different sodium bisulfite concentrations were prepared by dilution of the stock solutions. Sodium chloride was used to maintain the total sodium ion concentration constant. In order to stabilize the bisulfite solutions against oxygen oxidation, 1% (v/v) ethyl alcohol was added to the samples for the ionic strength dependence study. Concentrations of sodium bisulfite in solution were determined by adding the sample to excess triiodide solution and back-titrating with thiosulfate.<sup>(6)</sup>

Ultraviolet measurements were made on Cary 14 and 118 spectrophotometers using quartz cells equipped with ground glass stoppers with path lengths of 10, 5, 1, 0.5, 0.1, 0.05, and 0.01 cm. Samples for Raman measurement were centrifuged at 8,000 rpm in a Servall Superspeed RC-2 centrifuge for at least one-half hour in order to eliminate suspended matter. Raman spectra were recorded on a J-Y Optical Systems Ramanor HG-2 spectrometer, using a Coherent Radiation CR-3 Ion Laser line at 514.5 nm. Rectangular fluorimeter cells of 1 cm path length equipped with teflon fitted covers were used for Raman measurements. To prevent air oxidation, all solutions were prepared and loaded into spectrophotometric cells in a nitrogen atmosphere glove bag.

In order to measure relative Raman intensities, an internal standard was used. The water band at  $3400 \text{ cm}^{-1}$  was tried until it was found that its shape and intensity are sensitive to halide ions.<sup>(7,8)</sup> The actual measurements were all made relative to the symmetric stretch of  $0.5 \text{ M ClO}_4^-$  at  $936 \text{ cm}^{-1}$ . In some cases,  $0.5 \text{ M NaClO}_4$  was present as the internal standard

when the Raman measurement of  $\text{HSO}_3^-$  was made. In other cases, the bisulfite intensity was referenced to water at  $3400 \text{ cm}^{-1}$  in the absence of perchlorate, and then referenced to perchlorate by measurements of water relative to perchlorate in a solution of the same composition except that  $0.5 \text{ M NaClO}_4$  replaced the corresponding concentration of  $\text{NaCl}$ . The two types of measurement agreed well.

The Raman intensities were measured by setting the spectrometer at the proper wavenumber and recording the intensity on a chart for about 15 seconds. The wavenumber setting was quickly switched back and forth between the reference and sample positions, usually six times for each sample. Measurements were made only after the laser had warmed up for at least 15 minutes and settled to a constant intensity.

In the Raman measurements at low concentrations of bisulfite, the water contributed a large Raman background which was not completely reproducible. The following procedure was used to obtain the intensity of the  $\text{HSO}_3^-$  band. The Raman intensity of the solution was measured not only at  $2532 \text{ cm}^{-1}$ , but also at  $2432$  and  $2632 \text{ cm}^{-1}$  where the H-S band has fallen to a low but not negligible value. A blank solution of the same composition, except with sodium chloride replacing the sodium bisulfite, was measured at the same three wavenumbers, and these three intensities were subtracted from the corresponding three intensities of the sample. The resulting two intensities at  $2432$  and  $2632 \text{ cm}^{-1}$  were averaged and the average subtracted from the difference at  $2532 \text{ cm}^{-1}$  to yield a value proportional to the Raman intensity of the  $\text{HSO}_3^-$ . In this procedure, it is assumed that the emissivity arises from  $\text{HSO}_3^-$ ,  $\text{H}_2\text{O}$  and an unknown, irreproducible source (probably fluorescent impurities) and that the intensity of the latter is linear between  $2432$  and  $2632 \text{ cm}^{-1}$ .

Results: Since the method required no assumption about constancy of  $Q_d$ , it became possible to work at high concentrations of bisulfite ion where a significant fraction is converted to the dimer. Experiments were first attempted at a maximum concentration of 2 M  $\text{NaHSO}_3$  and at a constant sodium concentration of 2 M, but the effects were too small to yield reliable results. The majority of the experiments were done at a total concentration of 5 M  $\text{Na}^+$  with  $\text{NaCl}$  replacing  $\text{NaHSO}_3$ . The concentration of sodium ion was kept constant with the idea in mind that the three negative ions of interest,  $\text{S}_2\text{O}_5^{2-}$ ,  $\text{HSO}_3^-$ , and  $\text{ClO}_4^-$  would be most affected by the positive ions in the solution; thus activity coefficient changes and changes in Raman emissivities and  $a_d$  would be minimized.

An attempt was made to determine the sensitivity of the  $\text{ClO}_4^-$  Raman band to solution composition. Comparison was made of the perchlorate  $936\text{ cm}^{-1}$  band for a set of solutions containing 0.50 M  $\text{NaClO}_4$  and sodium bisulfite concentrations ranging from 4.5 to 0.144 M and each with the appropriate  $\text{NaCl}$  concentration to give 5.0 M total sodium ion. The measurements were performed by taking readings at  $936\text{ cm}^{-1}$  of a solution using the 1 cm fluorimeter cell, carefully removing the contents of the cell without moving it and replacing with pure water, which was in turn measured at  $3400\text{ cm}^{-1}$ . No mirrors were used to enhance the light collection. Results were reproducible to a few percent. The data are shown in Table 2. No significant change appears in the molar intensity, indicating that the Raman intensity of  $\text{ClO}_4^-$  is not strongly dependent on solution composition under conditions somewhat similar to those used in the bisulfite experiments.

A similar comparison for the  $2532\text{ cm}^{-1}$  intensity of two ca. 0.06 M bisulfite solutions, one containing 4.9 M  $\text{NaCl}$  and the other 4.9 M  $\text{NaClO}_4$ , gave average ratios of  $i$  at  $2532\text{ cm}^{-1}$  to  $i$  at  $3400$  of pure water of 0.063

and 0.61 respectively. These agree within the experimental accuracy and show no marked sensitivity of the Raman intensity of the H-S band to the anion.

For the determination of  $Q_d$ , three series of experiments were run on bisulfite solutions, all at approximately 5 M  $\text{Na}^+$ . The Raman data for the series prepared from  $\text{Na}_2\text{S}_2\text{O}_5$  are shown in Table 3. Values of  $\frac{I_{2532}}{[\sum \text{HSO}_3^-] I_{936}}$ , where  $I_{936}$  is the intensity of the perchlorate standard, are plotted versus  $[\sum \text{HSO}_3^-]$  in Fig. 1 as the circles. The decrease in the ordinate with increasing bisulfite concentration is due to conversion of more than half of the bisulfite to  $\text{S}_2\text{O}_5^{2-}$  at the highest concentration.

The optical absorbance of  $\text{S}_2\text{O}_5^{2-}$  at 320 nm was measured for a series of corresponding solutions. Values of  $[\text{HSO}_3^-]$  were calculated for each of these for a set of assumed molar absorptivities of  $\text{S}_2\text{O}_5^{2-}$  as described under "Method." A semi-log of the resulting family of curves of  $\frac{[\text{HSO}_3^-]}{[\sum \text{HSO}_3^-]}$  versus  $[\sum \text{HSO}_3^-]$  was superimposed on the plot of the Raman data and moved vertically until the best fit of each to the Raman data was achieved. Three such curves are shown in Fig. 1. The center curve with  $a_d = 26.5$  has been positioned to give a "best fit," while the other two curves are drawn with the same ordinate intercept, rather than displaced to give "best fits," in order to avoid a jumble of crossed lines. From the fitting, one deduces that a molar absorbance value of 26.5 fits best. It is to be noted that the fitting is quite sensitive to the value of the molar absorbance.

Two other series of Raman and UV experiments were run in which the solutions were prepared by bubbling  $\text{SO}_2$  into 5 M NaOH. Unfortunately, there was some uncertainty in the pH of the solutions and therefore, a precise correction could not be made for the  $\text{SO}_3^{2-}$  present. The values of  $a_d$  obtained, however, were not very sensitive to this correction and varied from

26 to 28 and 27 to 28 respectively, depending on the size of the correction made. We take the value of  $a_d = 26.5 \pm 1.0$  from the  $\text{Na}_2\text{S}_2\text{O}_5$  series as the best value.

Having determined the "best value" for  $a_d$  at 320 nm, the values of  $Q_d$  for the UV measurements of Fig. 1 can be calculated to see how much  $Q_d$  varied over the solution composition range studied. These results are shown in Table 4 along with the corresponding values calculated assuming  $a_d$  at 320 nm equal to 25.5 and 27.5. All three sets have appreciable trends in  $Q_d$ , increasing percentagewise with decreasing  $a_d$ . The results show that any method which depended on the assumption of constancy of  $Q_d$  for deducing its value from the optical absorption data of this set of solutions would lead to quite erroneous values of  $a_d$  and  $Q_d$ .

Once having obtained the value of  $a_d$  at 320 nm, the molar absorbance of  $\text{S}_2\text{O}_5^{2-}$  at any other wavelength could be determined. The value at the absorption maximum at 255 nm was found to be  $(5.79 \pm 0.10) \times 10^3$ .

If one assumes that the molar absorbance of  $\text{S}_2\text{O}_5^{2-}$  is constant, independent of solution composition, an optical absorbance measurement immediately gives the concentration of  $\text{S}_2\text{O}_5^{2-}$ . Thus the value of  $Q_d$  can be determined readily for any solution. Measurements were made of  $Q_d$  as a function of ionic strength with NaCl or  $\text{NaClO}_4$ <sup>(9)</sup> as the electrolyte, as shown in Fig. 2.

As judged from the optical absorbance, the temperature dependence of  $Q_d$  is small. Because the Raman measurements are quite laborious, and temperature control difficult, no attempt was made to determine  $a_d$  at another temperature. Instead, it was assumed that  $a_d$  was temperature independent, and values of  $Q_d$  of 0.132, 0.126, .117, and .111 were calculated from absorbance data at 25, 35, 45, and 55°C at an ionic strength of 2.1 M and 1% ethanol. The calculated apparent  $\Delta H$  for the dimerization reaction is then -1.1 kcal and the entropy of dimerization at 25° is -8 e.u. for these experimental conditions.

### Discussion

In the next to last column of Table 4 are tabulated the values of  $Q_d$  with  $a_d = 26.5$ . It is seen that  $Q_d$  does change appreciably over the range of solution composition studied, even though the  $\text{Na}^+$  concentration was held nearly constant.

The  $Q_d$  values found are roughly one third as large as those reported by Bourne et al.<sup>3</sup> for similar solution compositions, as may be seen by comparison of Fig. 2 with the data of Table 1. That the molar absorptivity they used is too small is readily confirmed by the observation that the apparent molar absorptivity of  $\text{S}_2\text{O}_5^{2-}$  at 255 nm of the 5 M  $\text{NaHSO}_3$  solution of Table 1 was already 66 percent greater than their reported molar absorptivity of  $\text{S}_2\text{O}_5^{2-}$ . If one recalculates the absorbance data of Bourne et al. using our molar absorptivity, the  $Q_d$  values are in good agreement with those found here, including their Fig. 1 data on ionic strength dependence.

The ionic strength dependence of  $Q_d$  is presumably dominated by the rapidly decreasing activity coefficient of the doubly charged  $\text{S}_2\text{O}_5^{2-}$ . As a result, the dimerization becomes much more important at high ionic strength.

#### Identification of $\text{S}_2\text{O}_5^{2-}$ and bisulfite Raman Bands

Simon and co-workers,<sup>(10)</sup> Herlinger and Long,<sup>(11)</sup> and Davis and Chatterjee<sup>(12)</sup> have attempted to assign to either bisulfite ion or  $\text{S}_2\text{O}_5^{2-}$  all of the observed Raman bands in aqueous solutions containing these species in equilibrium. We have made quantitative measurements of the intensity of these bands as a function of the bisulfite concentration in order to identify more certainly those belonging to bisulfite and to  $\text{S}_2\text{O}_5^{2-}$ , respectively. Semi-log plots of the intensity versus  $[\Sigma \text{HSO}_3^-]$  generally showed that  $i/[\Sigma \text{HSO}_3^-]$  decreased rapidly with decreasing  $[\Sigma \text{HSO}_3^-]$ , just as does the ultraviolet absorption of

$S_2O_5^{2-}$ , or increased slowly to a finite value with decreasing  $[\Sigma HSO_3^-]$ , as expected for a bisulfite band (e.g., the  $2532\text{ cm}^{-1}$  band in Fig. 1). An exception was the band at  $1052\text{ cm}^{-1}$  which decreased slowly to a finite value as  $[\Sigma HSO_3^-]$  decreased to zero. Obviously this band is a superposition of a band from  $S_2O_5^{2-}$  and a band from bisulfite ion. Representative plots are shown in Fig. 3, including the  $1052\text{ cm}^{-1}$  band. From such plots it is concluded that there are bisulfite bands at  $467^{(13)}$ ,  $506$ ,  $587$ ,  $730$ ,  $1021$ ,  $1052$ ,  $1128$ , and  $2532\text{ cm}^{-1}$ , and  $S_2O_5^{2-}$  bands at  $234$ ,  $309$ ,  $425$ ,  $556$ ,  $655$ ,  $966$ ,  $1052$ , and  $1170\text{ cm}^{-1}$ . The assignments agree with those of Davis and Chatterjee,<sup>(12)</sup> Herlinger and Long,<sup>(11)</sup> and Simon et al.<sup>(10)</sup> except in the following cases:

- (1) Our results show that the  $1052\text{ cm}^{-1}$  band, previously assigned to  $S_2O_5^{2-}$ , is actually a superposition of a  $S_2O_5^{2-}$  band and a bisulfite band.
- (2) Simon reported a very weak band at  $1089\text{ cm}^{-1}$  which was attributed to both bisulfite and  $S_2O_5^{2-}$ , but we see no evidence of such a band. Long gives a band at  $1085\text{ cm}^{-1}$  assigned only to  $S_2O_5^{2-}$ , but it must have been deduced only through curve resolution. Davis places a  $S_2O_5^{2-}$  band at  $1071\text{ cm}^{-1}$ , again apparently using curve resolution since the published spectrum shows no clear-cut evidence of the band. Solid salts of  $S_2O_5^{2-}$  show a Raman band around  $1085\text{ cm}^{-1}$  (14,15). We conclude that a  $S_2O_5^{2-}$  band may be detectable by curve resolution, but there is no reliable evidence for a bisulfite band in this region.
- (3) Long reports bands at  $168$ ,  $200$ ,  $395$ ,  $637$ ,  $685$ ,  $740$ ,  $1085$ ,  $1196$ ,  $2494$ , and  $2543\text{ cm}^{-1}$  which apparently were obtained by curve-resolving asymmetric bands. No one else has attempted such resolutions except Davis for the  $2532\text{ cm}^{-1}$  band and the weak  $1071\text{ cm}^{-1}$  band they reported.
- (4) The weak band at  $506\text{ cm}^{-1}$ , on dilution, appears to behave as bisulfite in contrast to the conclusion of Simon and Long that it belongs to the dimer.
- (5) Our concentration dependence plot for the weak  $587\text{ cm}^{-1}$  band shows no evidence of  $S_2O_5^{2-}$  while Long and Simon report this band as belonging to both bisulfite and dimer.
- (6)

Both Long and Davis decomposed the  $2532 \text{ cm}^{-1}$  band into three separate bands, but with quite different positions and intensities. We found no evidence for more than a single band on varying separately the temperature, concentration of bisulfite and pH, results which are quite inconsistent with Long's explanation of the source of the three postulated bands.

Structure of bisulfite ion: Two plausible structures for bisulfite ion are



Simon and Waldmann<sup>(16,17)</sup> showed many years ago by Raman detection of the H-S vibration that species I was present in aqueous solution as well as in solid  $\text{RbHSO}_3$  and  $\text{CsHSO}_3$ .<sup>(18)</sup> Vibrational assignments of the latter compounds have been made by Meyer, Peter and Shaskey-Rosenlund.<sup>(14)</sup>

For aqueous solutions, in the S-O stretching region there are four clearly observed bands belonging to bisulfite ion. One of these at  $1128 \text{ cm}^{-1}$  is actually the H-S bending motion of species I as shown by deuterium substitution, and in agreement with Myers et al's<sup>(14)</sup> assignment for solid  $\text{CsHSO}_3$ . The other three are strong bands occurring at 1052, 1021, and  $730 \text{ cm}^{-1}$ . Bisulfite species I has  $\text{C}_{3v}$  symmetry and therefore should have only two S-O stretching frequencies, as observed in  $\text{CsHSO}_3$ . The presence of a third strong band which appears not to be an overtone or combination band, leads to the conclusion that another form of bisulfite besides species I must be present. Presumably this is species II.

Since no band near  $730 \text{ cm}^{-1}$  is present in  $\text{CsHSO}_3$  where the bisulfite is in the form of species I, the  $730 \text{ cm}^{-1}$  band is assigned to species II, presumably the S-O stretch of S-O-H. The remaining two bands at 1052 and



and  $1021 \text{ cm}^{-1}$  belong one each to species I and II, but one cannot tell which. They are symmetric stretches of the S-O configurations. The asymmetric S-O stretch of species I is presumably too weak to be observed, as might be expected from the  $\text{CsHSO}_3$  Raman spectrum.<sup>(14)</sup> The same is probably true for the species II asymmetric stretch. Polarization measurements of each of the three bands are in agreement with the assignments.

It is of interest to compare the position of the two bands that can be assigned to bisulfite species II with the Raman bands reported<sup>(19,20)</sup> for  $\text{HSeO}_3^-$ , which is believed to have the proton attached to an oxygen. The three Se-O stretching bands are at  $615$ ,  $\sim 790$  (weak), and  $855 \text{ cm}^{-1}$ . The ratio of the wavenumber of the lowest Se-O stretching band to the lowest S-O stretching band is  $0.842$ . If one uses this same factor to divide the highest Se-O frequency, one predicts  $1015 \text{ cm}^{-1}$  for the corresponding S-O band, a value close to the two possible assignments for species II at  $1052$  or  $1021 \text{ cm}^{-1}$ , and therefore in reasonable agreement.

We believe that the definite identification of three S-O stretching frequencies for bisulfite ion provides direct experimental evidence for bisulfite species II in aqueous solution. The literature contains much speculation on its possible existence.<sup>(21)</sup> Simon and co-workers,<sup>(10)</sup> from their Raman measurements of bisulfite solutions, concluded that both isomers of bisulfite ion were present in aqueous solution at appreciable concentrations.<sup>(22)</sup> They cited two lines of evidence that species II is present in addition to species I, which is unambiguously identified by the H-S vibration at  $2532 \text{ cm}^{-1}$ . First, they found seven Raman bands attributable to bisulfite species, whereas species I,  $\text{H-SO}_3^-$ , has only six fundamental bands. Secondly, they argued that the band at  $709 \text{ cm}^{-1}$  did not fit with frequencies predicted for species I

from comparisons with the Raman spectra of  $\text{CH}_3 - \text{SO}_3^-$  and  $\text{C}_2\text{H}_5 - \text{SO}_3^-$ , while it was consistent with a frequency expected for species II,  $\text{SO}_2 - \text{OH}^-$ , based on an extrapolation from  $\text{SO}_2 - \text{O} - \text{CH}_3^-$ . The first line of evidence can be disputed because one of the Raman lines cited, the line at  $1089 \text{ cm}^{-1}$ , probably does not exist in that our measurements, using a laser light source, show no evidence of such a line, nor did Long et al report a line at this frequency. Thus Simon et al in actuality had only six Raman lines that could be attributed to bisulfite ion since they did not recognize that the line at  $1050 \text{ cm}^{-1}$  was a superposition of a bisulfite and a  $\text{S}_2\text{O}_5^{2-}$  line.

The argument that a line at  $709 \text{ cm}^{-1}$  line could not be attributed to species I we believe to be valid, although subject to some uncertainty because it is based on comparisons with other compounds. Presumably it is the S-O stretch of the S-O-H configuration in species II, as argued by Simon and Kriegsmann. (10)

It may be noted that appreciable concentrations of bisulfite species II are not unexpected on the basis of its acid ionization constant. Kossiakoff and Harker's (23) treatment of ionization constants of oxygenated acids with the proton on the oxygen leads to a predicted  $K_a$  of species II of  $10^{-7}$ . Since the observed ionization constant of bisulfite ion is of the order of  $10^{-7}$ , there should be an appreciable concentration of species II in bisulfite solutions. (It might be noted than an extension of the argument then leads to the prediction of a  $K_a$  of  $\text{SO}_2$  of  $5 \times 10^{-3}$  and thus appreciable concentration of  $\text{SO}(\text{OH})_2$  in solutions of  $\text{SO}_2$ , although none has been detected by Raman or other measurements.)

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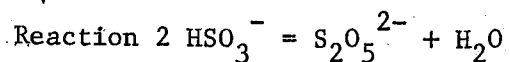
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Table 1. Literature Values of the Equilibrium Quotient  $Q_d$  for the



Temp., °C	Ionic Strength	$a_{\text{S}_2\text{O}_5^{2-}}$	$Q_d$	Investigator
20	0.07 to 0.32 M	$4 \times 10^3$ (255 nm)	0.07 M	Golding <sup>1</sup>
22	0.18 M	142.9 (258) nm)	2.0	Arkhipova and Chistyakova <sup>2</sup>
25.0	2.0	1980 (255 nm)	0.34	Bourne, Higuchi and Pitman <sup>3</sup>
	0	1980 (255 nm)	0.076	

Table 2. Test of the Constancy of the  $\text{ClO}_4^-$  Raman Emissivity at  $936 \text{ cm}^{-1}$  with Respect to Solution Composition. All Solutions Contained  $0.50 \text{ M NaClO}_4$ .

$\Sigma \text{ S(IV)}^*$	$\text{Cl}^-$ *	$\frac{I_{936}}{[\text{ClO}_4^-] \times I_{3400} \text{ (pure water)}}$
4.56 M	0 M	1.27
4.10	0.40	1.30
3.07	1.43	1.31
2.05	2.45	1.34
1.02	3.48	1.28
0.512	3.99	1.28
0.277	4.22	1.29
0.144	4.36	1.29

\*The S(IV) and  $\text{Cl}^-$  were added as  $\text{Na}_2\text{S}_2\text{O}_5$  and  $\text{NaCl}$  respectively. Total sodium concentration was  $5.0 \text{ M}$  except for first solution.

Table 3. Raman Intensities of 2532  $\text{cm}^{-1}$  Band of Bisulfite Solutions

$\Sigma \text{S(IV)}^{\text{a}}$	NaOH, M	$\Sigma \text{Na}^+$ , M <sup>c</sup>	$\Sigma \text{HSO}_3^-^{\text{b}}$	$\frac{I_{2532}}{[\Sigma \text{HSO}_3^-] I_{936}}^{\text{d}}$
4.79	0.250	5.04	4.54	4.20
3.90	0.203	5.10	3.69	4.59
2.93	0.153	5.09	2.78	5.18
1.923	0.100	5.02	1.823	6.20
0.996	0.0520	5.05	0.944	7.45
0.496	0.0259	5.02	0.470	8.02
0.2523	0.0132	5.02	0.2391	8.85

<sup>a</sup> $[\Sigma \text{S(IV)}]$  is concentration of total sulfur in +4 oxidation state as determined by triiodide titration. The S(IV) was added as  $\text{Na}_2\text{S}_2\text{O}_5$ .

<sup>b</sup> $[\Sigma \text{HSO}_3^-] = [\text{HSO}_3^-] + 2[\text{S}_2\text{O}_5^{2-}]$

<sup>c</sup>The total sodium concentration was maintained nearly constant by the addition of sodium chloride.

<sup>d</sup> $I_{2532}$  and  $I_{936}$  are the Raman emissivity of the solutions at the  $2532\text{cm}^{-1}$   $\text{HSO}_3^-$  band and the emissivity at  $936\text{cm}^{-1}$  of  $0.5\text{M ClO}_4^-$ , respectively. See Experiment.

Table 4. Variation of  $Q_d$  with Solution Composition for UV Data of Fig. 1.

$\Sigma S(IV), M^a$	NaOH, M	$\Sigma HSO_3^-, M$	$\Sigma Na^+, M^b$	$\frac{A}{l}$	$Q_d$		
					$a_d=25.5$	$a_d=26.5$	$a_d=27.5$
4.94	0.252	4.69	5.19	35.3	0.337	0.326	0.286
3.92	0.200	3.72	5.13	25.4	0.334	0.295	0.263
2.92	0.149	2.77	5.08	16.80	0.312	0.281	0.255
1.946	0.099	1.847	5.06	9.23	0.287	0.263	0.243
0.973	0.0497	0.923	5.05	2.93	0.239	0.224	0.211
0.505	0.0258	0.479	5.06	0.963	0.232	0.220	0.209
0.243	0.0124	0.230	5.03	0.253	0.224	0.214	0.205
0.0955	0.0049	0.0906	5.03	0.0452	0.234	0.224	0.215

<sup>a</sup>The S(IV) was added as  $Na_2S_2O_5$ .

<sup>b</sup>The total sodium ion concentration was maintained nearly constant by the addition of sodium chloride.

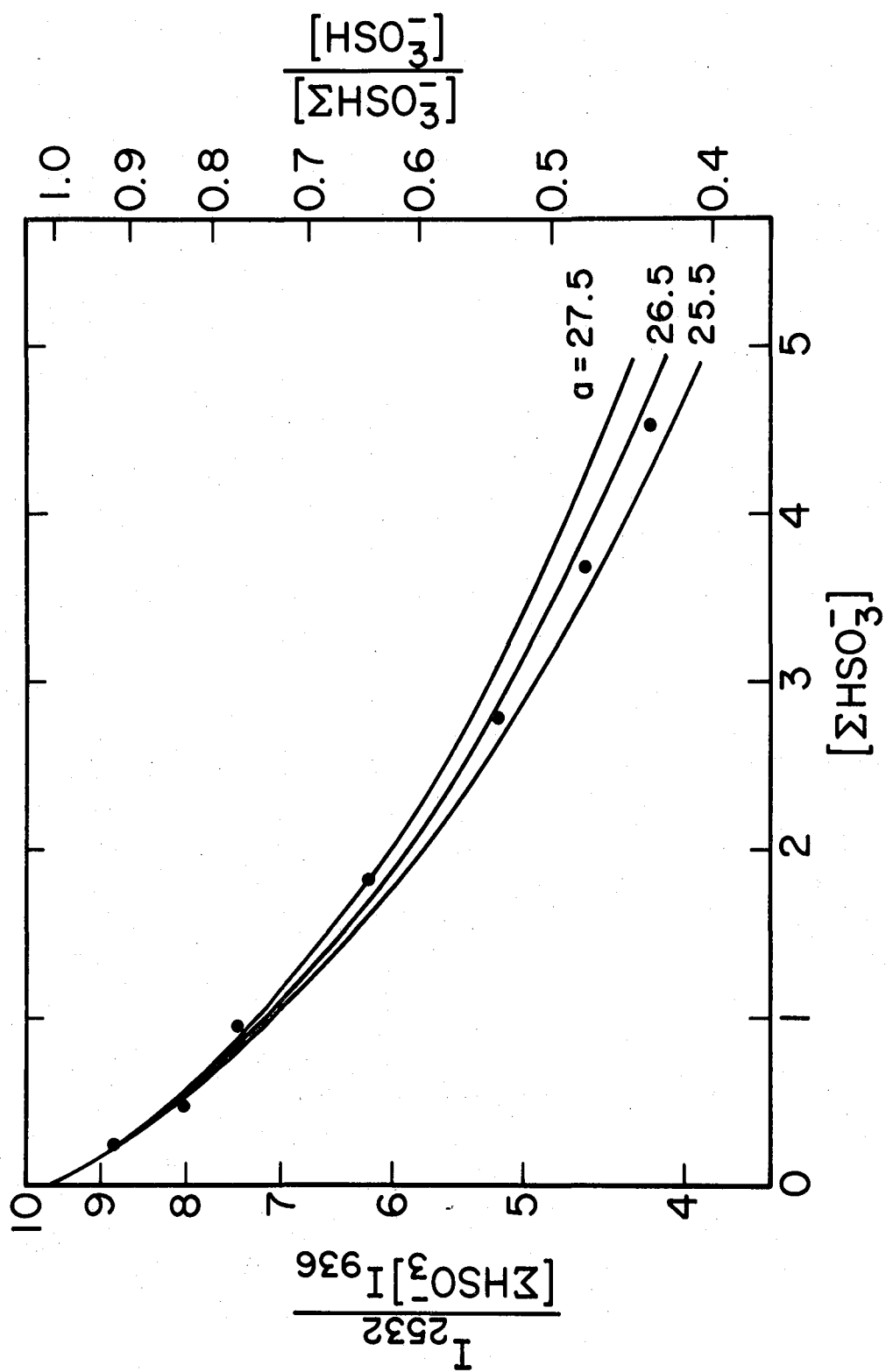


Legend for Figures

Fig. 1. Points show Raman data of Table 3. Solid lines represent  $[\text{HSO}_3^-]/[\Sigma\text{HSO}_3^-]$  calculated from the ultraviolet absorption at 320 nm assuming values for the molar absorptivity of  $\text{S}_2\text{O}_5^{2-}$  of 25.5, 26.5 and 27.5, respectively. The solid curves have been shifted vertically to give the best fit with the Raman points for the molar absorptivity of 26.5.

Fig. 2. Values of  $Q_d$  as a function of square root of ionic strength for solutions of NaCl and  $\text{NaClO}_4$ . The total concentration of  $\text{NaHSO}_3$  ranged from  $10^{-2}$  to  $10^{-1}$  M, and solutions contained sufficient NaOH to convert 5 percent of the  $\text{HSO}_3^-$  to  $\text{SO}_3^-$ . One volume percent ethanol was present to inhibit the oxidation of  $\text{HSO}_3^-$  by oxygen. The solid line is the Debye-Hückel limiting slope.

Fig. 3. Variation of apparent molar Raman emissivity of selected lines as a function of  $[\Sigma\text{HSO}_3^-]$ . To facilitate comparison the curves have been normalized to values of unity at 4.3 M  $\Sigma\text{HSO}_3^-$  by multiplication of the ordinate values by constant factors F. Values of F are 0.083, 0.019 and 0.020 for 1021, 1052, and  $234\text{ cm}^{-1}$ . The data are not precise because of large overlap corrections from neighboring lines.



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Figure 1

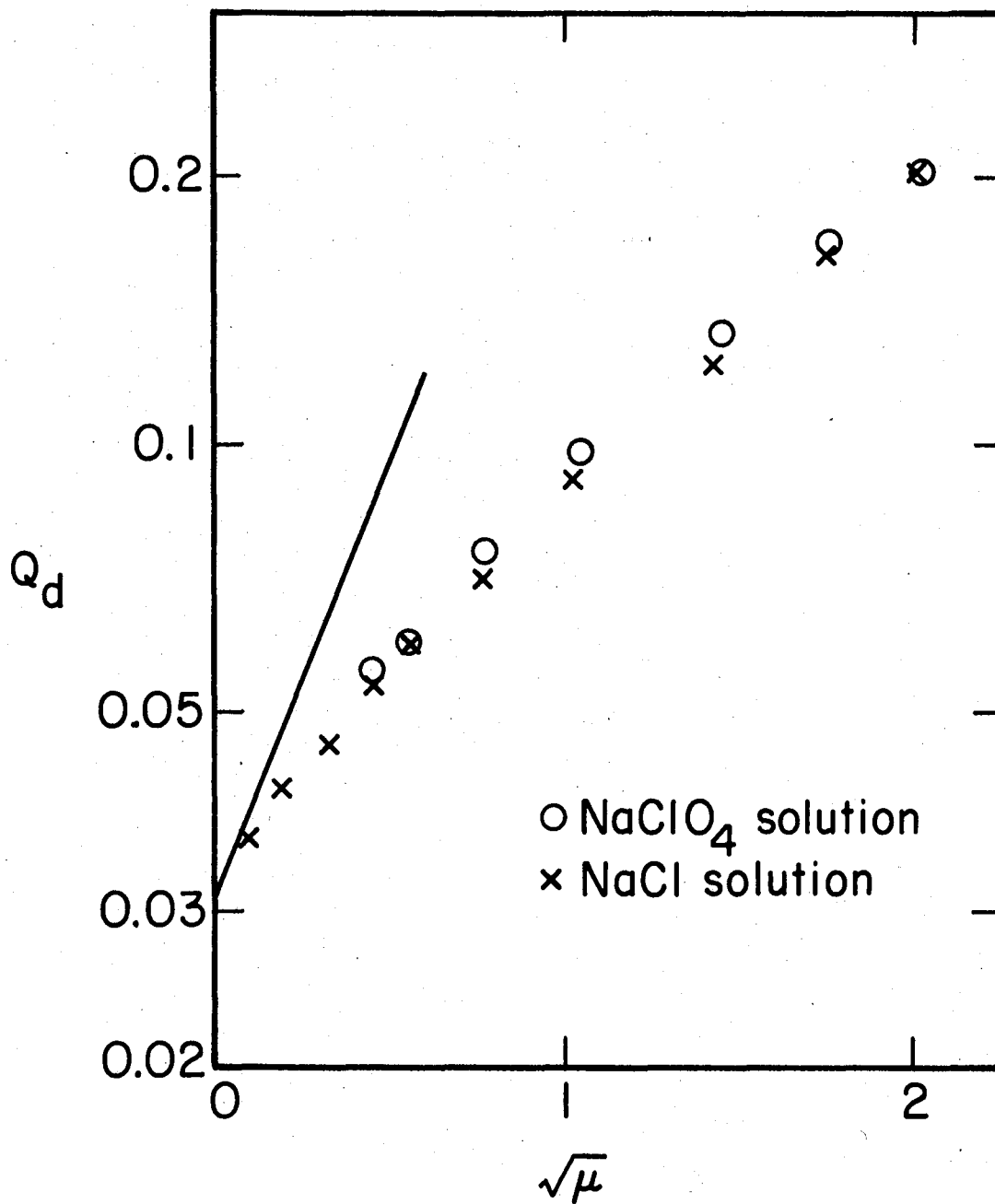


Figure 2

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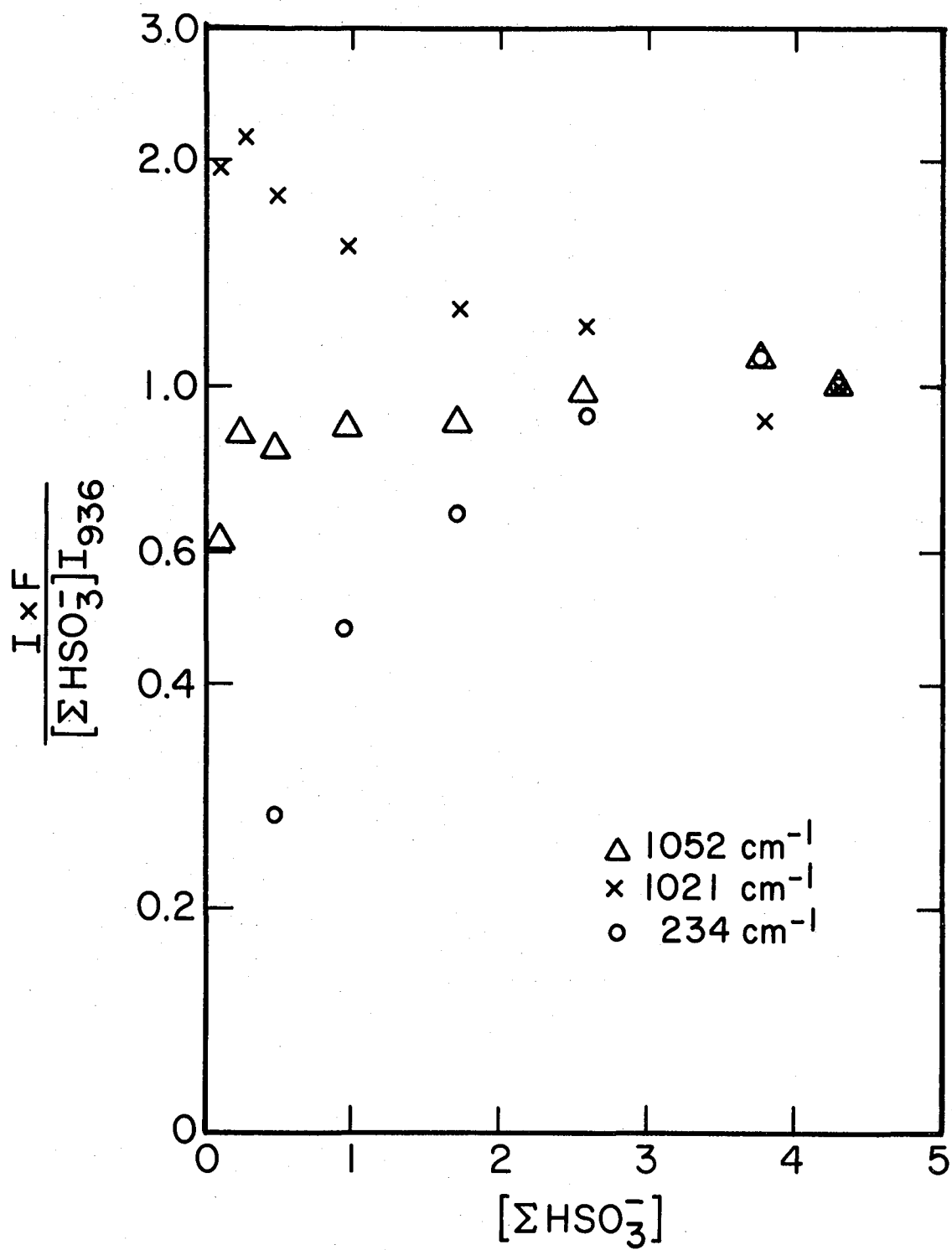


Figure 3

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