sampling loop attached to a high-vacuum manifold was used in conjunction with a 2 m × $^1/_8$ in. SS Porapak Q column followed by a 1 m × $^1/_8$ in. SS Molecular Sieve 5A column. A Carle Model 5521 switching valve was situated between the columns. Valve switching during analyses avoided contamination of the zeolite column by CO_2 or H_2O.

Acknowledgment. The financial support of this work through NSF Grant CHE-7706792 is gratefully acknowledged.

Registry No. $[Ru^{III}(bpy)_3]^{3+}$, 18955-01-6; $[Ru^{II}(bpy)_3]^{2+}$, 15158-62-0; $[Ru^{II}(bpy)_3]Cl_2$, 14323-06-9.

Contribution from the Department of Chemistry and the Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Equilibrium Constant for the Dimerization of Bisulfite Ion To Form $S_2O_5^{2-}$

ROBERT E. CONNICK,*[1] THOMAS M. TAM, and ECKART VON DEUSTER

Received February 25, 1981

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. A value of Q_d of 0.088 M^{-1} was found for a dilute solution of bisulfite in 1 M $NaClO_4$ solution at 25 °C. 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.

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

$$2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O \qquad Q_d = [S_2O_5^{2-}]/[HSO_3^-]^2$$

Although several investigators[2,3] have attempted to measure Q_d, the results are far from concordant, as shown in Table I, 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 $S_2O_5^{2-}$ in a region where 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 $S_2O_5^{2-}$. To obtain reliable values for these parameters, it is necessary to convert an appreciable fraction of the total bisulfite to the dimer at the highest concentration studied. A reexamination of Golding's[2a] data shows no evidence of appreciable conversion. Arkhipova and Chistyakova[2b] investigated such a small concentration range that their results could give no meaningful information on fraction conversion. Bourne et al.[3] made a careful study at constant ionic strength and applied corrections for the presence of SO_2 and SO_3^{2-}. At their highest bisulfite concentration, 0.160 M, their interpretation of the data yielded 5% conversion to the disulfite dimer. But a 5% 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 redeterming Q_d a method was sought which would not require the assumption of constant Q_d over the range of solution composition studied.

Table I. Literature Values of the Equilibrium Quotient Q_d for the Reaction $2HSO_3^- \rightleftarrows S_2O_5^{2-} + H_2O$

temp, °C	ionic strength, M	$a_{S_2O_5^{2-}}$ (wavelength, nm)	Q_d, M	investigator
20	0.07-0.32	4 × 10^3 (255)	0.07	Golding[2a]
22	0.18	142.9 (258)	2.0	Arkhipova and Chistyakova[2b]
25.0	2.0	1980 (255)	0.34	Bourne, Higuchi, and Pitman[3]
	0	1980 (255)	0.076	

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 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-cm^{-1} band should be directly proportional to the concentration of bisulfite ion:[4]

$$I = i[HSO_3^-] \qquad (1)$$

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

$$[\Sigma HSO_3^-] = [HSO_3^-] + 2[S_2O_5^{2-}] \qquad (2)$$

---

(1) To whom correspondence should be addressed at the Department of Chemistry.

(2) (a) R. M. Golding, *J. Chem. Soc.*, 3711 (1960); (b) G. P. Arkhipova and I. I. Chistyakova, *Zh. Prikl. Khim.* (*Leningrad*), **44**, 2193 (1971).

(3) D. W. A. Bourne, T. Higuchi, and I. H. Pitman, *J. Pharm. Sci.*, **63**, 865 (1974).

(4) For convenience, the symbol HSO_3^- will be used to represent the sum of the concentrations of the two isomers.

0020-1669/82/1321-0103$01.25/0

was plotted on a semilog plot vs. the total bisulfite concentration, $[\sum HSO_3^-]$.

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

$$A = a_d l[S_2O_5^{2-}]$$

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:

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

A plot of $[HSO_3^-]$ divided by $[\sum HSO_3^-]$ on a semilog plot vs. $[\sum HSO_3^-]$ 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. When a family of curves for different assumed values of a_d is plotted and compared with the shape of the curve from the Raman data, the one giving the best fit corresponds to the "correct" choice of a_d. With 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 Results section.

Experimental Section

Sodium pyrosulfite and sodium hydroxide (analytical grade), sodium chloride (reagent grade), and sodium perchlorate (reagent grade) were used as supplied by Mallinckrodt Chemical and G. Frederick Smith Chemical Co. 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 SO_2 gas through a 5 M NaOH solutoin until the pH of the solution approached 5.5. In the former case, sufficient NaOH was added to convert 5 mol % of the total bisulfite to sulfite ion to reduce the SO_2 concentration and discharge the yellow color.[5] 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. So that the bisulfate solutions could be stabilized 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.[6]

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 8000 rpm in a Servall Superspeed RC-2 centrifuge for at least 0.5 h 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. So that air oxidation could be prevented, all solutions were prepared and loaded into spectrophotometric cells in a nitrogen atmosphere glovebag.

So that relative Raman intensities could be measured, an internal standard was used. The water band at 3400 cm^{-1} was tried until it was found that its shape and intensity are sensitive to halide ions.[7,8] The actual measurements were all made relative to the symmetric stretch of 0.5 M ClO_4^- at 936 cm^{-1}. In some cases, 0.5 M $NaClO_4$ was present as the internal standard when the Raman measurement of HSO_3^- was made. In other cases, the bisulfite intensity was referenced to water at 3400 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 M $NaClO_4$ replaced the corresponding concentration of NaCl. The two types of measurement agreed well.

Table II. Test of the Constancy of the ClO_4^- Raman Emissivity at 936 cm^{-1} with Respect to Solution Composition[a]

$[\Sigma S^{IV}]$,[b] M	$[Cl^-]$,[b] M	$I_{936}/[ClO_4^-]I_{3400}$(pure H_2O)
4.56	0	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

[a] All solutions contained 0.50 M $NaClO_4$. [b] The S^{IV} and Cl^- were added as $Na_2S_2O_5$ and NaCl, respectively. Total sodium concentration was 5.0 M except for first solution.

The Raman intensities were measured by setting the spectrometer at the proper wavenumber and recording the intensity on a chart for about 15 s. 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 min 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 HSO_3^- band. The Raman intensity of the solution was measured not only at 2532 cm^{-1} but also at 2432 and 2632 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 cm^{-1} were averaged and the average subtracted from the difference at 2532 cm^{-1} to yield a value proportional to the Raman intensity of the HSO_3^-. In this procedure, it is assumed that the emissivity arises from HSO_3^-, H_2O, and an unknown, irreproducible source (probably fluorescent impurities) and that the intensity of the latter is linear between 2432 and 2632 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 $NaHSO_3$ 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 Na^+ with NaCl replacing $NaHSO_3$. The concentration of sodium ion was kept constant with the idea in mind that the three negative ions of interest, $S_2O_5^{2-}$, HSO_3^-, and 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 ClO_4^- Raman band to solution composition. Comparison was made of the perchlorate 936-cm^{-1} band for a set of solutions containing 0.50 M $NaClO_4$ and sodium bisulfite concentrations ranging from 4.5 to 0.144 M and each with the appropriate NaCl concentration to give 5.0 M total sodium ion. The measurements were performed by taking readings at 936 cm^{-1}

---

(5) Concentrated solutions of bisulfite ion contain a small amount of SO_2 which interacts with the bisulfite to form a yellow species. Its constitution will be discussed in a future publication.

(6) I. M. Kolthoff and R. Belcher, "Volumetric Analysis", Vol. 3, Interscience, New York, 1957, 293.

(7) A. Naomichi and I. Mitsuto, *J. Raman Spectrosc.*, **7**, 161 (1978).

(8) J. W. Schultz and D. F. Hornig, *J. Phys. Chem.*, **65**, 2131 (1961).

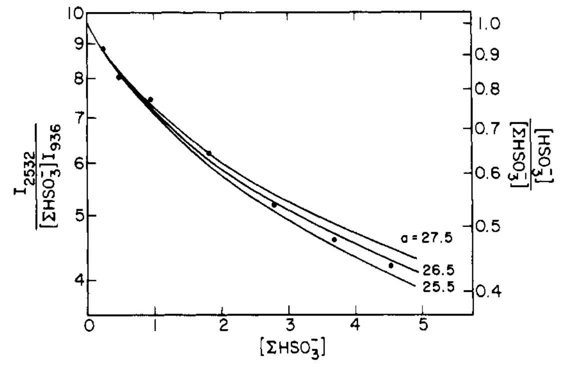

Figure 1. Points show Raman data of Table III. Solid lines represent $[HSO_3^-]/[\sum HSO_3^-]$ calculated from the ultraviolet absorption at 320 nm with the assumption of values for the molar absorptivity of $S_2O_5^{2-}$ of 25.5, 26.5 and 27.5, respectively. The solid curves have been shifted vertically to give the best fit with the Raman points for the molar absorptivity of 26.5.

Table III. Raman Intensities of 2532-cm^{-1} Band of Bisulfite Solutions

$[\Sigma S^{IV}]$[a]	[NaOH], M	$[\Sigma Na^+]$,[c] M	$[\Sigma HSO_3^-]$,[b] M	$I_{2532}/[\Sigma HSO_3^-]I_{936}$[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

[a] $[\Sigma S^{IV}]$ is concentration of total sulfur in +4 oxidation state as determined by triiodide titration. S^{IV} was added as $Na_2S_2O_5$. [b] $[\Sigma HSO_3^-] = [HSO_3^-] + 2[S_2O_5^{2-}]$. [c] The total sodium concentration was maintained nearly constant by the addition of sodium chloride. [d] I_{2532} and I_{936} are the Raman emissivity of the solutions at the 2532-cm^{-1} HSO_3^- band and the emissivity at 936 cm^{-1} of 0.5 M ClO_4^-, respectively; see Experimental Section.

of a solution with use of 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 cm^{-1}. No mirrors were used to enhance the light collection. Results were reproducible to a few percent. The data are shown in Table II. No significant change appears in the molar intensity, indicating that the Raman intensity of 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-cm^{-1} intensity of two ca. 0.06 M bisulfite solutions, one containing 4.9 M NaCl and the other 4.9 M $NaClO_4$, gave average ratios of *i* at 2532 cm^{-1} to *i* at 3400 of pure water of 0.063 and 0.061, 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 Na^+. The Raman data for the series prepared from $Na_2S_2O_5$ are shown in Table III. Values of $I_{2532}/[\sum HSO_3^-]I_{936}$ where I_{936} is the intensity of the perchlorate standard, are plotted vs. $[\sum HSO_3^-]$ in Figure 1 as the circles. The decrease in the ordinate with increasing bisulfite concentration is due to conversion of more than half of the bisulfate to $S_2O_5^{2-}$ at the highest concentration.

The optical absorbance of $S_2O_5^{2-}$ at 320 nm was measured for a series of corresponding solutions. Values of $[HSO_3^-]$ were calculated for each of these for a set of assumed molar absorptivities of $S_2O_5^{2-}$ as described in the Method section. A semilog plot of the resulting family of curves of $[HSO_3^-]/[\sum HSO_3^-]$ vs. $[\sum HSO_3^-]$ 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 Figure 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 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 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 $Na_2S_2O_5$ series as the best value.

After the "best value" for a_d at 320 nm is determined, the values of Q_d for the UV measurements of Figure 1 can be calculated to see how much Q_d varied over the solution composition range studied. These results are shown in Table IV along with the corresponding values calculated with the assumption of 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 the value of a_d at 320 nm is obtained, the molar absorbance of $S_2O_5^{2-}$ 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 $S_2O_5^{2-}$ is constant, independent of solution composition, an optical absorbance measurement immediately gives the concentration of $S_2O_5^{2-}$. 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 $NaClO_4$[9] as the electrolyte, as

Table IV. Variation of Q_d with Solution Composition for UV Data of Figure 1

					Q_d		
$[\Sigma S^{IV}]$,[a] M	[NaOH], M	$[\Sigma HSO_3^-]$, M	$[\Sigma Na^+]$,[b] M	*A*/*l*	$a_d = 25.5$	$a_d = 26.5$	$a_d = 27.5$
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

[a] S^{IV} was added as $Na_2S_2O_5$. [b] The total sodium ion concentration was maintained nearly constant by the addition of sodium chloride.

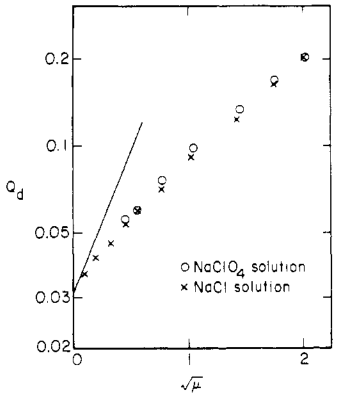

Figure 2. Values of Q_d as a function of square root of ionic strength for solutions of NaCl and $NaClO_4$. The total concentration of $NaHSO_3$ ranged from 10^{-2} to 10^{-1} M, and solutions contained sufficient NaOH to convert 5% of HSO_3^- to SO_3^-. One volume percent ethanol was present to inhibit the oxidation of HSO_3^- by oxygen. The solid line is the Debye–Hückel limiting slope.

shown in Figure 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 is 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, 0.117, and 0.111 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 ΔH for the dimerization reaction is then −1.1 kcal and the entropy of dimerization at 25 °C is −8 eu for these experimental conditions.

Discussion

In the next to last column of Table IV 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 Na^+ concentration was held nearly constant.

The Q_d values found are roughly one-third as large as those reported by Bourne et al.[3] for similar solution compositions, as may be seen by comparison of Figure 2 with the data of Table I. That the molar absorptivity they used is too small is readily confirmed by the observation that the apparent molar absorptivity of $S_2O_5^{2-}$ at 255 nm of the 5 M $NaHSO_3$ solution of Table I was already 66% greater than their reported molar absorptivity of $S_2O_5^{2-}$. 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 Figure 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 $S_2O_5^{2-}$. As a result, the dimerization becomes much more important at high ionic strength.

Identification of $S_2O_5^{2-}$ and Bisulfite Raman Bands. Simon and co-workers,[10] Herlinger and Long,[11] and Davis and Chatterjee[12] have attempted to assign to either bisulfite ion or $S_2O_5^{2-}$ 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 $S_2O_5^{2-}$, respectively. Semilog plots of the intensity vs. $[\sum HSO_3^-]$ generally showed that $i/[\sum HSO_3^-]$ decreased rapidly with decreasing $[\sum HSO_3^-]$, just as the ultraviolet absorption of $S_2O_5^{2-}$ does, or increased slowly to a finite value with decreasing $[\sum HSO_3^-]$, as expected for a bisulfite band (e.g., the 2532-cm^{-1} band in Figure 1). An exception was the band at 1052 cm^{-1} which decreased slowly to a finite value as $[\sum HSO_3^-]$ decreased to 0. 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 Figure 3, including the 1052-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 cm^{-1} and $S_2O_5^{2-}$ bands at 234, 309, 425, 556, 655, 966, 1052, and 1170 cm^{-1}. The assignments agree with those of Davis and Chaterjee,[12] Herlinger and Long,[11] and Simon et al.[10] except in the following cases. (1) Our results show that the 1052-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 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 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 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 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 cm^{-1} which apparently were obtained by curve-resolving asymmetric bands. No one else has attempted such resolutions except Davis for the 2532-cm^{-1} band and the weak 1071-cm^{-1} band they reported. (4) The weak band at 506 cm^{-1}, on dilution, appears to behave as bisulfite in contrast to the conclusion of Simon and Long that it belongs

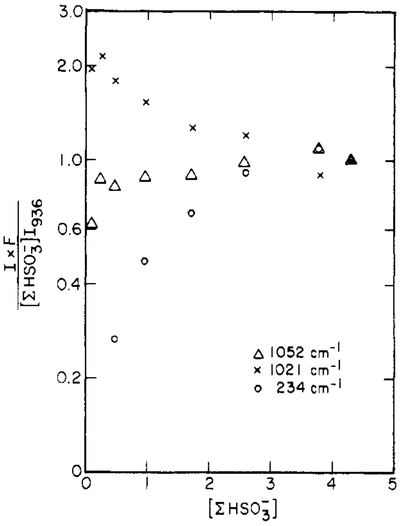

Figure 3. Variation of apparent molar Raman emissivity of selected lines as a function of $[\sum HSO_3^-]$. So that a comparison could be facilitated, the curves have been normalized to values of unity at 4.3 M $\sum HSO_3^-$ by multiplication of the ordinate values by constant factors F. Values of F are 0.083, 0.019, and 0.020 for 1021, 1052, and 234 cm^{-1}. The data are not precise because of large overlap corrections from neighboring lines.

---

(9) We are indebted to Mark Lipshutz for the $NaClO_4$ solution measurements.

(10) A Simon and H. Kriegsmann, *Chem. Ber.*, **89**, 2442 (1956), and earlier papers by Simon and co-workers cited therein.

(11) A. W. Herlinger and T. V. Long, II, *Inorg. Chem.*, **8**, 2661 (1969).

(12) A. R. Davis and R. M. Chatterjee, *J. Solution Chem.* **4**, 399 (1975). In their Table II, the authors state that their assignments were actually taken from ref 11.

(13) This weak band was overlapped so strongly by the 425-cm^{-1} band that it was difficult to be sure of its intensity.

(14) B. Meyer, L. Peter, and C. Shaskey-Rosenlund, *Spectrochim. Acta, Part A*, *35A*, 345 (1979).

(15) A. Simon, K. Waldmann, and E. Steger, *Z. Anorg. Allg. Chem.*, **288**, 131 (1956).

to the dimer. (5) Our concentration dependence plot for the weak 587-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-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 HSO_3^- where the proton is attached to the sulfur and $HOSO_2^-$ where the proton is attached to one of the oxygens. Simon and Waldmann[16,17] showed that HSO_3^- exists in aqueous solution as well as in $RbHSO_3$ and $CsHSO_3$[18] by observing the H–S Raman band. Vibrational assignments of the latter compounds have been made by Meyer, Peter, and Shaskey-Rosenlund.[14]

In aqueous solution, in addition to the H–S bend of HSO_3^- at 1128 cm^{-1},[14] there are three detectable Raman bands belonging to bisulfite ion in the S–O stretching region: 1052, 1021, and 730 cm^{-1}. None of these appears to be combinations or overtones. Since HSO_3^- has C_{3v} symmetry, it should have only two S–O stretching frequencies. Therefore, it is concluded that another bisulfite species must be present, presumably $HOSO_2^-$.

The 730-cm^{-1} band is assigned to the S–O stretch of the H–O–S group in $HOSO_2^-$ because no such band is present in $CsHSO_3$.[14] The symmetric stretches at 1052 and 1021 cm^{-1} belong one each to the two bisulfite species, but one cannot tell which. The asymmetric stretches are probably too weak to be observed, as might be expected from the $CsHSO_3$ Raman spectrum.[14] Polarization measurements of the three bands are consistent with these assignments.

A comparison can be made of the $HOSO_2^-$ frequencies[19,20] with those of biselenite ion which is believed to be $HOSeO_2^-$. Three bands are observed at 615, ~790 (weak), and 855 cm^{-1}. The ratio of the lowest frequencies of the selenium and sulfur species is 615/730 = 0.842. Dividing the highest frequency of the $HOSeO_2^-$ by this factor yields a predicted value of 1015 cm^{-1} for the corresponding S–O band, a value in reasonable agreement with either the observed 1021- or 1052-cm^{-1} bands.

We believe the definite identification of three S–O stretching frequencies for bisulfite ion provides the most direct evidence for the presence of $HOSO_2^-$ in aqueous solution. The literature contains much speculation on its possible existence.[21] Simon and co-workers[10] concluded from Raman data that both isomers were present.[22] They cited two lines of evidence that $HOSO_2^-$ was present in addition to HSO_3^-. First, they reported seven Raman bands for bisulfite species, while HSO_3^- should have only six. This evidence can be disputed, however, because their band at 1089 cm^{-1} was not detected in our measurements with a laser light source nor was it reported by Herlinger and Long.[11]

The second line of reasoning was that the 709-cm^{-1} band did not fit with frequencies predicted for HSO_3^- by comparison with the Raman spectrum of $CH_3SO_3^-$ and $C_2H_5SO_3^-$, while it was consistent with a frequency predicted for $HOSO_3^-$ by extrapolation from the spectrum of $CH_3OSO_2^-$. We believe this argument to be valid, although subject to some uncertainty because it is based on comparisons with other compounds.

Appreciable concentrations of $HOSO_2^-$ 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 this species 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 $HOSO_2^-$ in bisulfite solutions. (It might be noted that an extension of the argument then leads to the prediction of a K_a for sulfurous acid of 5×10^{-3} and thus appreciable concentration of $SO(OH)_2$ in solutions of SO_2, although none has been detected by Raman or other measurements.)

Acknowledgment. We wish to express our appreciation to Mark Lipshutz for making the ionic strength measurements of Q_d in sodium perchlorate solutions. This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Research, Advanced Environment Control Division of the U.S. Department of Energy, under Contract number W7405 ENG-48 through the Morgantown Energy Technology Center, Morgantown, WV.

Registry No. HSO_3^-, 15181-46-1; $S_2O_5^{2-}$, 23134-05-6.

---

(16) A. Simon, *Angew. Chem.*, **59**, 247 (1947).

(17) A. Simon and K. Waldmann, *Z. Anorg. Allg. Chem.*, **281**, 113 (1955).

(18) A. Simon and W. Schmidt, *Z. Electrochem.*, **64**, 737 (1960).

(19) G. E. Walrafen, *J. Chem. Phys.*, **36**, 90 (1962).

(20) A. Simon and R. Paetzold, *Z. Anorg. Allg. Chem.*, **303**, 46 (1960).

(21) "Gmelins Handbuch der Anorganischen Chemie", Sulfur, Part B2, 8th ed., 1960, pp 403, 422, 425–427, 461–62.

(22) Simon apparently did not consider the evidence entirely conclusive as in his last publication on the subject he stated that the question of the $HOSO_2^-$ was still open. (A. Simon and R. Paetzold, *Z. Electrochem.*, **64**, 209 (1960)).

(23) A. Kossiakoff and D. Harker, *J. Am. Chem. Soc.*, **60**, 2047 (1938).