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Structure and ionization of sulfuric acid in water

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Abstract

Newly recorded Raman spectra of aqueous sulfuric acid provide scattering shifts of very high sensitivity hence signal-to-noise ratios, at a broad concentration range, up to 17 M. I interpret the spectra as (a) providing no evidence for incomplete H₂SO₄ ionization at low concentration, (b) reflecting only one dissociation event below ~5 M, (c) indicating a gradual ion association at ~5 – 12.5 M, and (d) exhibiting further structural changes of the sulfate above 12.5 M. The analysis of the Raman shifts supports the postulated presence in solution of the *parabisulfate* anion HSO₅³⁻ as a sole sulfate ion up to ~5 M, as concluded before (D. Fraenkel, *J. Phys. Chem. B*, 2012, **116**, 11662; *ibid.*, 2012, **116**, 11678; *J. Chem. Thermodyn.*, 2014, **78**, 215), an ion association producing *parasulfuric acid*, H₄SO₅ between 5 and 12.5 M, and a dehydration of H₄SO₅ to H₂SO₄ above 12.5 M. These conclusions are rationalized and corroborated by (1) a correlation of the Raman spectra with well-known physicochemical properties of aqueous sulfuric acid, and (2) structural analogies between the proposed *parasulfates* and other related compounds and anions.

Keywords: acid, sulfuric, ionization, sulfur oxide, Raman scattering, aerosol, freezing

Introduction

Sulfuric acid – H_2SO_4 – is the world's most important industrial chemical;¹ it affects many fields of science and technology, such as storage batteries, fertilizer production, catalytic processes, ore and mineral dissolution and processing, resin manufacture, and more. The aqueous acid strongly impacts the environment, *e.g.*, as acid rain, and influences global climate in atmospheric aerosol.² It is therefore essential that we improve our knowledge and understanding of the structure and physicochemical behavior of the acid in water.

General background

In this article I continue an effort to shed new light on the nature of aqueous sulfuric acid. Previously, I revisited and analyzed (1) the ionic activity of aqueous sulfuric acid,³ (2) the acidity and base neutralization of the acid,⁴ and (3) the theoretical treatment of the acid by so-called thermodynamic models of electrolyte solutions.⁵ Based on the already reported evidence,^{3–5} aqueous sulfuric acid in the approximate concentration range 0 – 5 M behaves as a typical 1–3 strong electrolyte. A plausible explanation for this behavior is that the acid in water is H_4SO_5 (*parasulfuric acid*) fully dissociated, practically in one step, to three protons [as hydronium (H_3O^+) ions] and the trivalent anion HSO_5^{3-} (*parabisulfate ion*). In the current article, I inquire on whether spectroscopic and physicochemical evidence supports the idea that H_4SO_5 can indeed exist at >5 M, and that its conjugate base, HSO_5^{3-} is, as proposed, the dominant sulfate species in solution between 0 and ~ 5 M. A further aim of this work is to explore the essence and behavior of aqueous sulfuric acid at considerably higher concentration than ~ 5 M. Therefore, I now investigate the speciation of the aqueous acid, its

variation with concentration, and its influence on the physicochemical properties of the acid as relevant to bulk solutions and to aerosols.

The broad literature on aqueous sulfuric acid claims that the dissolved acid is a strong 1–1 electrolyte and a “moderately weak”⁶ 1–2 electrolyte hence it is H₂SO₄ dissociating to a mixture of H⁺, HSO₄⁻ and SO₄²⁻. This view is primarily based on the interpretation of Raman spectra of the acid. Therefore, in the current paper, I first revisit the Raman scattering shifts of aqueous sulfuric acid as reported in the literature, and reconsider their analysis. A major problem with the traditional Raman analysis is that it contradicts with the thermodynamic nature of aqueous H₂SO₄ as reflected by the change of the *mean ionic activity coefficient* (γ_{\pm} as molal) of the acid solution with acid concentration;^{3,5} this contradiction exists despite major literature sources claiming otherwise.^{6,7}

Old Raman studies

The structure of sulfuric acid and its ionization pattern in water has been deduced from Raman scattering spectra. In a 1949 review,⁸ Young and Blatz mentioned various Raman studies of the acid, but centered their attention on the spectral data of Rao.⁹ They offered a full analysis of the state of sulfuric acid in solution based on two fundamental assumptions:

- (1) Each spectral band in the S–O stretching vibration region corresponds to one distinct molecular or ionic species: the ~1055 cm⁻¹ band (1043 cm⁻¹ in the original work^{8,9}) to HSO₄⁻, the ~980 cm⁻¹ band to SO₄²⁻, and the ~900 (910^{8,9}) cm⁻¹ band to undissociated H₂SO₄.
- (2) Band intensity is proportional to the relative concentration of a species in solution.

Young and Blatz concluded that the acid comprises a 1:1 chemical combination of SO_3 and H_2O since they noticed that in the $\text{SO}_3\text{-H}_2\text{O}$ mixture, the 900 cm^{-1} scattering band passes a maximum in intensity at 50–50% mol. However, a close examination of the experimental data indicates that the 900 band maximum in Rao's work⁹ is, in fact, at ~40% mol SO_3 , thus apparently reflecting a different feature. [Young and Blatz did not consider, of course, the possibility that even if at high concentration, at the maximum intensity of the 900 cm^{-1} band, the acid is H_2SO_4 , it may transform to another acid structure at lower concentration before dissociating to ions (see below).] Echoing cited literature, Young and Blatz further concluded⁸ that the dissociation of H_2SO_4 in aqueous solution occurs in two steps, the first giving H^+ (as H_3O^+) and HSO_4^- , and the second – through further dissociation of $\text{HSO}_4^- - \text{H}^+$ and SO_4^{2-} . The complete ionization process was thus concluded to form two H^+ ions and one SO_4^{2-} ion per dissociated H_2SO_4 molecule. The second dissociation step was concluded to be weak, implying that sulfuric acid is approximately a 1–1 electrolyte, except at very high dilution ($<0.1\text{ M}$) where it gradually converts from 1–1 to 1–2 electrolyte. This view was later claimed to be supported by the behavior of the osmotic and activity coefficients of aqueous sulfuric acid solutions as functions of acid concentration.^{6,7} A further conclusion based on Raman spectroscopy,⁹ was that *H_2SO_4 is always present in solution* along with its ions, and it becomes the major species at higher concentration, $>5\text{ M}$. Therefore, at *any* concentration of the acid in water, the three sulfate species, HSO_4^- , SO_4^{2-} , and H_2SO_4 , all exist together, with the H^+ (H_3O^+) cations neutralizing the negative charge of the anions. In a further study,¹⁰ Young *et al.* derived relative HSO_4^- , SO_4^{2-} and H_2SO_4 concentrations based on the intensities of the respective Raman shifts, in the range 0.05 to ~18 M. Below 15 M,

they could not separate the 910 cm^{-1} band from the overlapping bands at 895 cm^{-1} (claimed to be due to HSO_4^-) and 980 cm^{-1} (claimed to be due to SO_4^{2-}). Rao⁹ observed the 910 cm^{-1} band at lower concentration but only above $\sim 9\text{ M}$, whereas earlier, researchers^{11–13} detected it even at $\sim 2\text{ M}$.

Newer Raman studies

Lund Myhre *et al.*¹⁴ have recently claimed that the HSO_4^- ion exhibits the “980 band”, as a major peak, in addition to the “1055 band”, and this is not due to partial dissociation of HSO_4^- to SO_4^{2-} , as erroneously claimed in the past;¹¹ the 980 band therefore represents both the HSO_4^- and SO_4^{2-} ions.¹⁴ Furthermore, the above authors also claimed that the HSO_4^- ion has twelve normal modes of vibration that are active in both Raman and infrared spectroscopies; there are nine normal vibrational modes in SO_4^{2-} .¹⁴ Moreover, the interpretation of the Raman spectra of aqueous sulfuric acid has recently become more refined through the studies of various research groups.^{15–17} The ~ 900 , ~ 980 and $\sim 1055\text{ cm}^{-1}$ bands are now assigned not to specific sulfate structures in their entirety, as in the past, but, respectively, to the ν_{SOH} “asymmetric stretching vibration of HSO_4^- ”, the ν_1 “total symmetric stretching vibration of SO_4^{2-} ”, and the ν_s “symmetric stretching vibration of HSO_4^- ”.¹⁵ This, however, has not changed researchers’ view on the general speciation of the acid in water^{14–17} since ν_{SOH} and ν_s are attributed to HSO_4^- and ν_1 to SO_4^{2-} . Thus, researchers still today associate the Raman scattering bands with specific ionic and molecular structures, and they all believe that in the S–O vibration region, the only possible sulfate species in aqueous solution of sulfuric acid are H_2SO_4 , HSO_4^- and SO_4^{2-} .

Purpose of this work

The literature's Raman analysis contradicts with the 1–3 electrolyte behavior of aqueous H_2SO_4 ; this contradiction needs to be addressed then resolved through an alternate analysis of the Raman spectral data. The analysis of Young and Blatz⁸ and the more recent data and their interpretation^{14–17} thus deserve close reexamination. In addition, the quality of the old Raman data of sulfuric acid is questionable and the newer data, based on much better spectral quality, have not been generated in a manner allowing a direct and straightforward comparison with the old data. Therefore, in the present work, Raman scattering spectra of aqueous sulfuric acid have been recorded again; this was done in a systematic and comparative manner and at a sufficiently broad concentration range. In light of the newly proposed structures of the acid and its ions in water, I now reexamine some anomalous properties of the aqueous acid^{18–22} and reveal parallels between the Raman scattering pattern and the peculiar change of the freezing point and electric conductivity of the aqueous acid as a function of concentration. Such parallels have hitherto never been noticed. I also point out a parallel between the Raman scattering bands and the apparent molal volume of aqueous sulfuric acid at varying acid concentration. Finally, I highlight some structural analogies between the proposed pentacoordinate sulfur oxides and known structures of related compounds and ions.

Experimental

Instrument

Raman scattering data were collected on an InPhotonics' fiber-optic portable InPhotote™ spectrometer (Model Number: INP-3b-785SR). The excitation source of the instrument is a frequency-stabilized 785-nm Class IIIb diode laser with maximum power output of 350 mW. The laser provides a CW (not pulsed) output less than 1 cm^{-1} wide about the maximum point. The entire spectral range is $328 - 1,976\text{ cm}^{-1}$ and the spectral resolution is $4 - 6\text{ cm}^{-1}$. The laser beam from the excitation fiber is collimated and passed through band-pass and dichroic filters prior to focusing it onto the solution sample, which is placed in an ordinary borosilicate vial. The back-scattered Raman signal is collimated by the same lens, reflected through a long-pass filter, and focused onto the collection fiber. Detection is done with a charge coupled device (CCD) detector. The spectrometer is controlled by a software package designed to negotiate with the laser source, probe and spectrograph.

Experimental detail

Spectra of aqueous sulfuric acid [ACS grade, 95% (nominal) solution in water, from Acros Organic, product 42452] diluted to various levels by de-ionized water, were recorded at $298 \pm 1\text{ K}$. The exact concentration of the initial acid was determined by titration with NaOH and found to be 16.8 M (90.6%) as the average of two consecutive tests. The net Raman shifts were obtained by subtracting the parallel spectra of pure de-ionized water (as blank, 0% acid) in the same kind of Pyrex vial, from the measured shifts of the acid samples. 16 samples of different acid concentrations, from 0.005 to 16.8 M , were measured under identical experimental conditions, in the spectral range $350 - 1900\text{ cm}^{-1}$. The two lowest concentration samples, of 0.005 and of 0.025 M , gave poor spectral quality and too low

signal-to-noise ratios, and therefore, they were not included in the subsequent analysis. Data collected by the instrument's software program were exported to and processed/analyzed by a MS Excel program.

Analytical treatment

For presenting the results on a common quantitative ground, all spectra have been normalized to 1.0 M. The composition of the main stretching vibration bands, at ~900, ~980 and ~1055 cm^{-1} , was calculated by measuring the areas of all three bands. Band intensity, in arbitrary units, has been then computed as the fraction of the particular band in the entire band composition, multiplied by the molar concentration of the acid. Peak frequency variations as functions of concentration, and peak frequency differences (e.g., stretching *vs.* bending modes), were obtained from the normalized spectra.

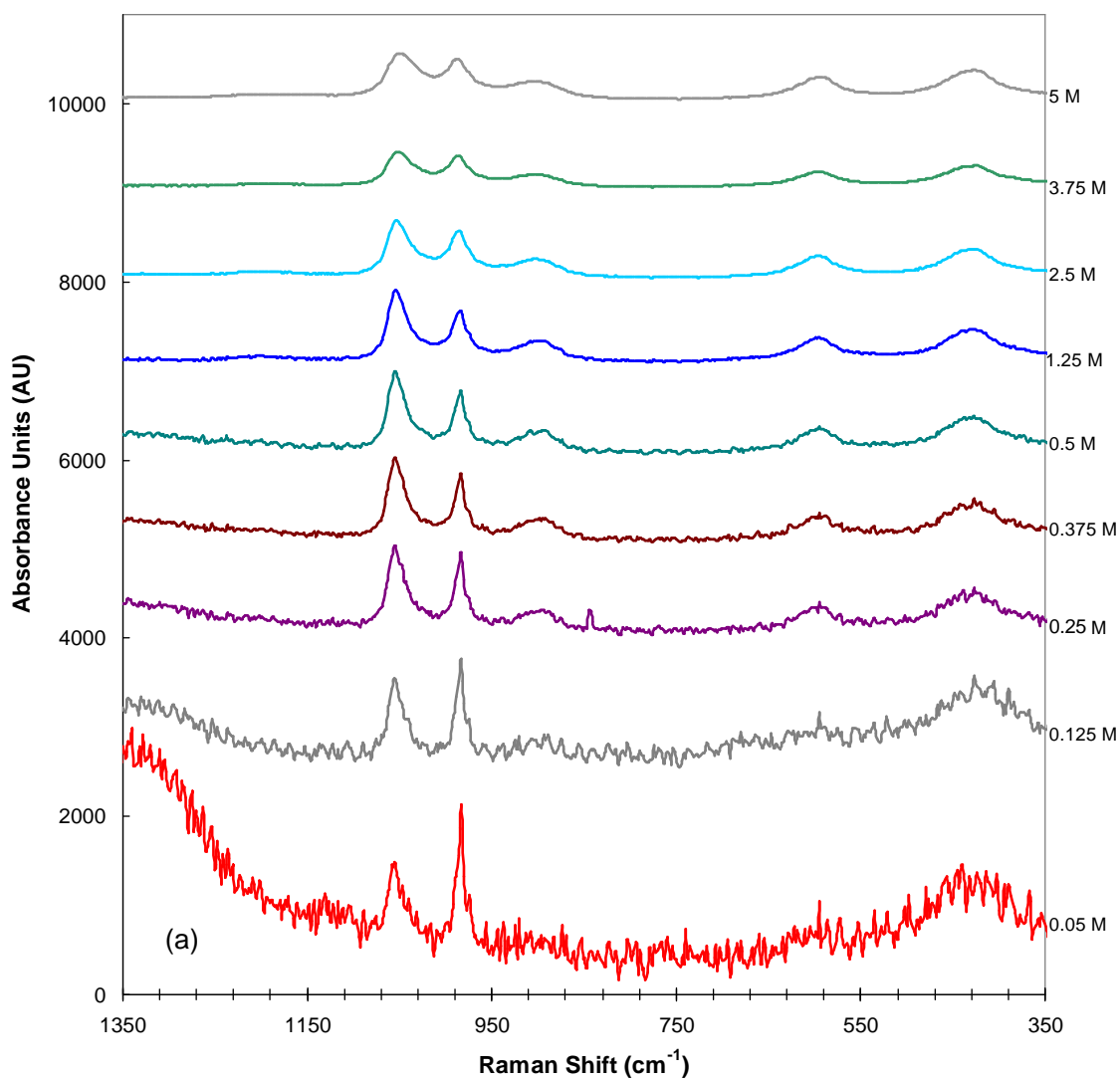
Results and discussion

Raman scattering of aqueous sulfuric acid

The results of the current Raman study are first presented in Figure 1 as net and normalized scattering bands, given as absorbance (relative) *vs.* wavenumber (cm^{-1}). Without specific details yet, two important findings clearly stand out:

- (1) The 900 band is present in the *entire* concentration range, and is detectable even at 0.05 M; however, the upward drift (blueshift) of this band suggests that it combines the known bands at ~890 and ~910 cm^{-1} (see below).

(2) About the same spectral combination of the 900, 980 and 1055 bands is maintained at least from 1 M to ~5 M; the normalized spectra in this M range thus look very similar to one another.



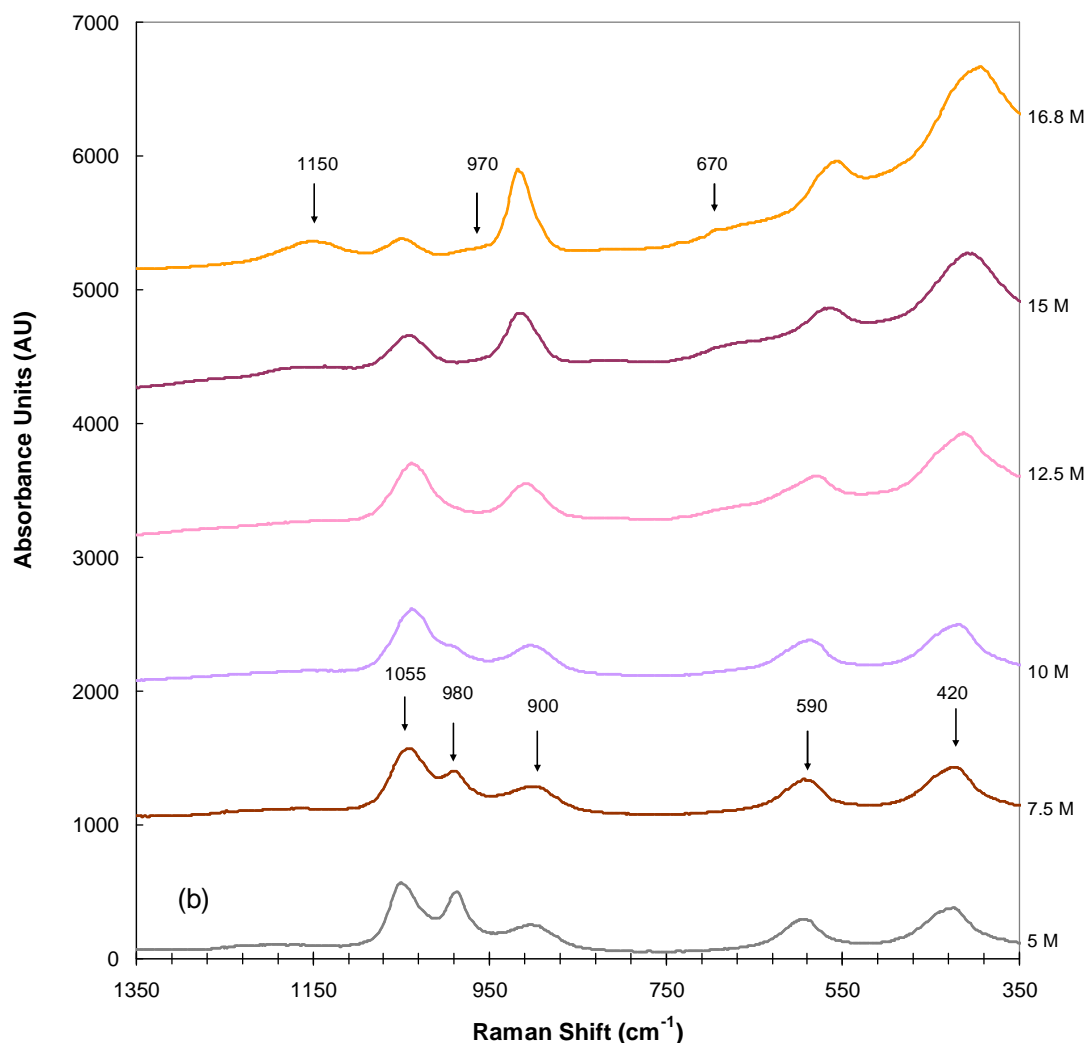


Fig. 1. Net Raman spectra of aqueous sulfuric acid, normalized to 1 M. The respective concentration is given right to each curve. The ordinate, in arbitrary units, is presented as a relative intensity scale. (Note the change in scale between Figure 1a and 1b, allowing better emphasis of the higher-concentration spectra.) (a) 0.05 – 5 M. The spectra at this concentration range are similar to one another, reflecting about the same pattern of ionic speciation. (b) 5 – 16.8 M. In this concentration range, the nature of the spectrum changes, indicating variations in ionic and molecular speciation. Arrows indicate the various sulfate scattering bands.

The new findings do not entirely agree with those of Young *et al.*¹⁰ and with the analysis of Young and Blatz.⁸ From the work of Young *et al.* it is not clear whether the 900 band was indeed detected below 15 M. The 900 and 980 bands were both practically undetected by Rao⁹ below 9 M, which can readily be blamed on the low sensitivity of the mercury arc Raman excitation source and the poor detection means used in the old Raman measurements.^{9,23} The laser excitation sources of modern Raman spectrographs are much more intense thus resulting in far higher spectral sensitivity; in addition, the detection of the scattered beam is far more efficient than the photoelectric methods and photographic plates used in the past.^{9,10} [A point of relevance: In Rao's experiments, each sample was exposed to the mercury arc beam for "exactly 5 hours" whereas in the present study (typical to modern Raman measurements) the sample's time of exposure to the laser beam was 15 seconds.] However, considering the differences in the Raman measurements, the present spectra do not significantly differ from the old spectra and they are quite similar to those reported more recently.^{14,15} But in the latter studies the measurements did not extend to very low concentration: Lund Myhre *et al.* reported¹⁴ "net" spectra (*i.e.*, with the water background subtracted) between 1.3 and 14.3 M, and Tomikawa and Kanno reported^{15a} "raw" spectra between 2.4 and 16.6 M. Also, the recent studies^{14,15} did not provide a quantitative analysis of the relative intensity of the 900 band and its frequency shift with concentration (see below).

Analysis of the new Raman data. As shown in Figure 1b, past ~5 M, the specific (*i.e.*, concentration-independent) intensity of the 900 band starts to grow strongly while that of the

980 band declines considerably and approaches zero above 12.5 M; the specific intensity of the 1055 band decreases above ~ 12.5 M but this band prevails even at 16.8 M. In fact, going from 5 M to ~ 12.5 M, there is a gradual transition between two distinct spectra, representing different intrinsic, or “pure”, states; that is, the 5 and 12.5 M spectra are of two different sulfate species. Therefore, spectra in the $\sim 5 - 12.5$ M range are superpositions of the 5 M and 12.5 M spectra, weighted for concentration changes, and they reflect a gradual transition from one sulfate structural state to another. This behavior cannot be reconciled with the peak assignments of Young and Blatz⁸ and of others.⁹⁻¹³ If each Raman band is assigned to a single species within the group H_2SO_4 , HSO_4^- and SO_4^{2-} , then one has to make the implausible assumption that the relative concentrations of these species remain about constant over orders of magnitude difference in total acid concentration. One also has to then make the unlikely conclusion that considerable amount of undissociated H_2SO_4 prevails even at and below 0.1 M. It is plausible, however, that the constant Raman spectral pattern below ~ 5 M, as reported here, represents a single sulfur oxyhydroxide species (see below).

The present results agree with those of Young *et al.*¹⁰ on three major features:

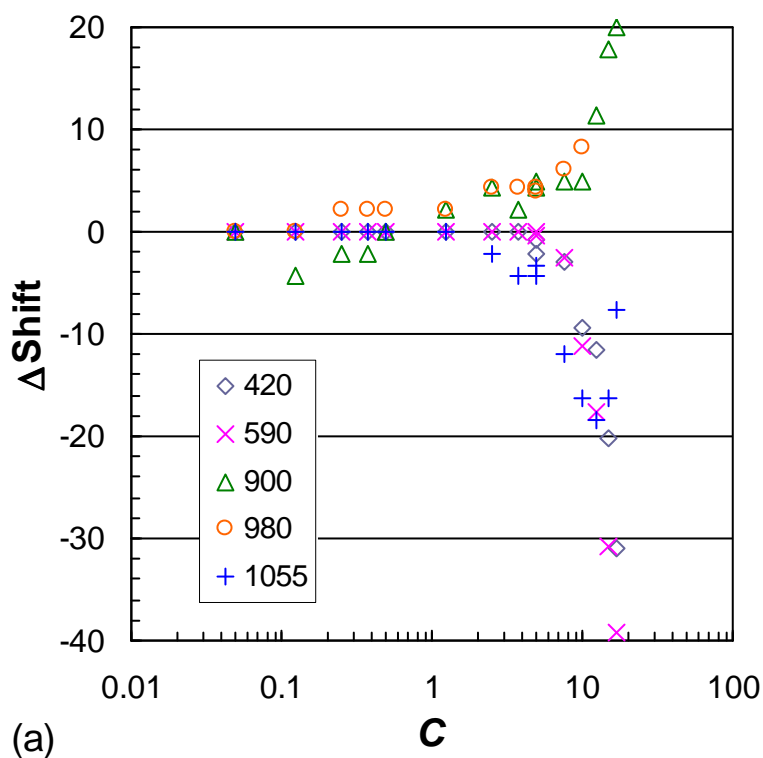
- (1) The relative (specific) intensity of the 1055 band is initially about constant, then passes a shallow maximum at ~ 13 M, followed by a considerable decline;
- (2) The relative intensity of the 980 band initially remains about constant up to ~ 5 M, but then declines sharply and eventually approaches zero at ~ 13 M; and
- (3) The 900 band intensity increases dramatically above ~ 15 M.

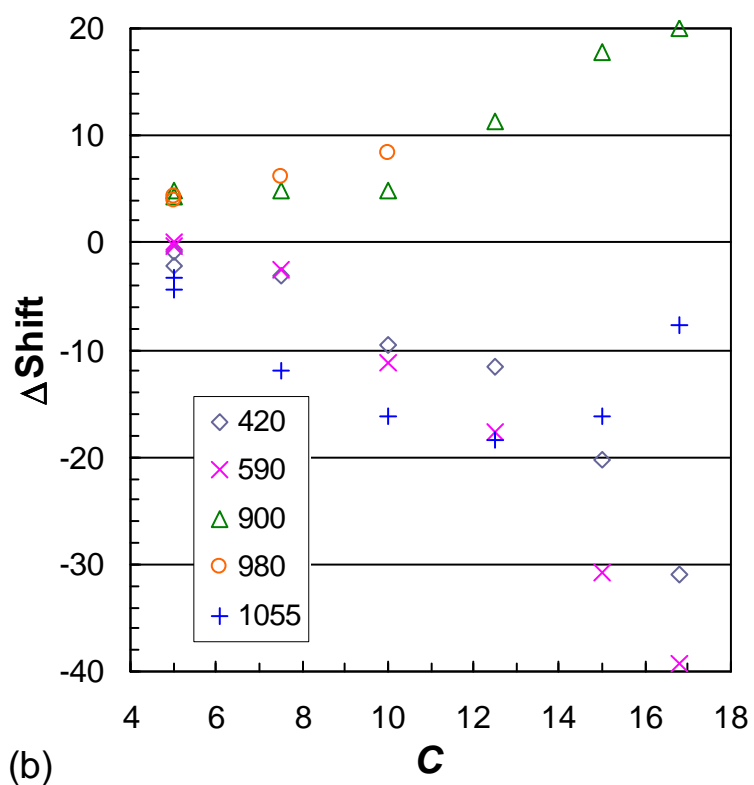
However, the new data differ from those of Young *et al.* in one critical fact: They show that the 900 band (apparently as a “890”–“910” combination, see below) exists not only

above 15 M but over the entire range of concentration. Some differences in peak intensities and peak ratios (but not in their trends) can be attributed to experimental and instrumental differences. Another significant feature of the current spectra is the appearance, at high concentration, of two new weak bands, at about 970 and 1150 cm^{-1} (Figure 1b). These bands were found previously,^{8,9,11-13} but were not reported by Young *et al.*¹⁰ An additional band is now detected at $\sim 670 \text{ cm}^{-1}$ and is observed only above 10 M (Figure 1b).

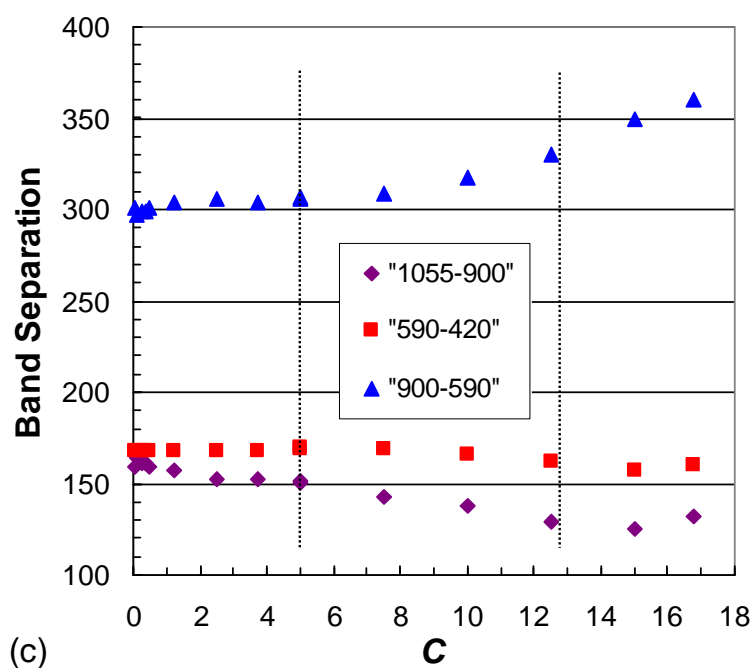
Figure 2 presents the frequency shifts of the major spectral bands of aqueous sulfuric acid in the 350 – 1350 cm^{-1} range. Because the instrument's spectral resolution is 4 – 6 cm^{-1} , band frequency shifts that are less than about 6 cm^{-1} cannot be considered meaningful. Also, because bands appear convoluted,¹⁴ frequency shifts, especially when small, should be regarded with caution. However, there is clear evidence for a systematic and gradual trend of frequency shift at high concentration. *All bands are essentially at constant frequency up to 5 M; they then shift considerably with increasing concentration.* The 900 and 980 bands experience a blueshift (i.e., shift to higher frequency) whereas the low-frequency 420 and 590 bands undergo a redshift (a drift to lower frequency); this reflects a different spectral nature between the higher-frequency and lower-frequency bands. The 1055 band is unique in initially shifting to lower frequency but then passing a frequency minimum (at $\sim 12.5 \text{ M}$) and going back toward its initial frequency value. This, as further clarified below, indicates that the 1055 band constitutes a combination of stretching vibrations of three different molecular/ionic segments; such vibrations are of the same type and somewhat varying from one another in their exact frequency. If the 1055 band represents three different species that transform sequentially from one to another (i.e., “1” \rightarrow “2” \rightarrow “3”) over the concentration

range 5 – 17 M, such that the first species dominates at 5 M, the second at 12.5 M and the thirds at 17 M, then if the 1055 band of the second species (“2”) is at somewhat lower frequency than those of the first and third species, a minimum in frequency of the 1055 band would occur at 12.5 M. It is thus plausible that a sulfur oxide species “2” gradually forms from “1” up to 12.5 M and then gradually transforms to another species, “3”, above 12.5 M (see below).





(b)



(c)

Fig. 2. Frequency shift (cm^{-1}) of Raman bands of aqueous sulfuric acid as a function of concentration, C (M). Symbol assignment to frequency or frequency difference is given in the insets. Frequency variation is with respect to 0.05 M acid solution. (a) Full C range. (b) C range, 4 – 17 M. (c) Band frequency difference (vertical dotted lines denote borders of region in which the main changes occur).

The frequency shifts shown in Figure 2a and 2b generally agree with those reported previously.^{11–13} However, those frequency shifts were not adequately explained in the literature. Figure 2c shows the pattern of selected band frequency differences. There is an especially strong change of the difference between the 1055 and 900 bands in the 5 – 13 M range and of the difference between the 900 and 590 bands in the range of about 5 – 17 M, corresponding to the major variations in spectral pattern (Figure 1b). In the former case, the bands move closer to each other; in the latter, they drift away from each other. In contrast, the 590–420 band couple maintains a more or less constant frequency difference at the entire concentration range of the present study.

The new Raman findings are summarized quantitatively in Figure 3 as approximate peak intensity composition against sulfuric acid concentration, considering only the 900, 980 and 1055 bands. Areas are cumulative relative net intensities of the respective shifts; along each vertical line, the length of a zone is its relative intensity. Vertical broken lines are approximate borders between different regimes (see Figure 2c), as specified above the figure frame. In the process of producing this presentation, experimental results were plotted then extracted by interpolation for each concentration of integer number, in the range 1 – 17 M.

For Rao's work⁹ (see below) the range was 3 – 17 M. Figure 3a marks three concentration regions of sulfuric acid in solution. In the first, up to ~5 M, there are no major changes in the pattern of the main three bands; in the second (~5 – 12.5 M), the 900 band increases and the 980 band decreases in relative intensity; and in the third region (>12.5 M), the 980 band is no longer present, the 900 band increases considerably, and the 1055 band decreases sharply. For comparison, Figure 3b is the parallel presentation of Rao's results⁹ used by Young and Blatz.⁸ The contrast between Figure 3a and 3b is obvious – in Rao's work, the 980 band was very weak at any concentration, and the 900 (910) band was relatively contributing only above 9 M. If in Figure 3a we disregard the 980 band and the 900 band below ~9 M, the similarity between Figure 3a and 3b becomes apparent, confirming that the main difference between the current results and Rao's is the improvement in instrument's spectral sensitivity in the present work (see above).

The effect of acid concentration on band intensity of the three main stretching vibration modes, is shown in Figure 4. As expected from Figure 3a, the intensities of all three bands increase about linearly with concentration up to 5 M. The 980 band intensity then passes a maximum and declines monotonously at higher concentration, becoming zero at ~13 M. The 1055 band intensity also passes a maximum but this maximum occurs at much higher concentration, ~12.5 M; it thus almost coincides with the disappearance of the 980 band. Unlike the intensities of the 980 and 1055 bands, that of the 900 band increases steadily with acid concentration without passing a maximum (up to 16.8 M) and the increase becomes steeper above ~12 M. The three concentration regions in Figure 4 are, of course, the same as

in Figures 2c and 3a, and the two borderlines between regions occur at band maxima: the first at the maximum of the 980 band and the second at the maximum of the 1055 band.

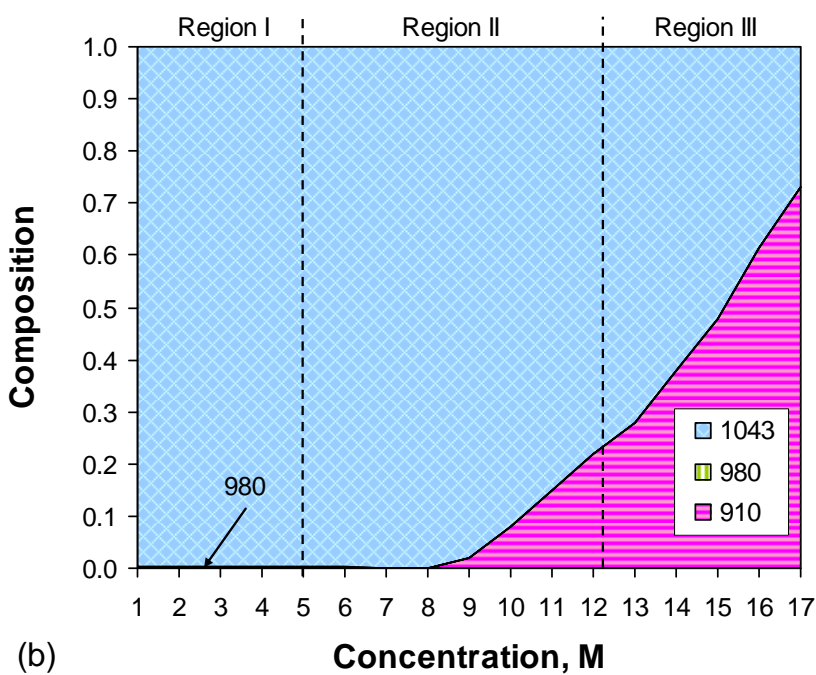
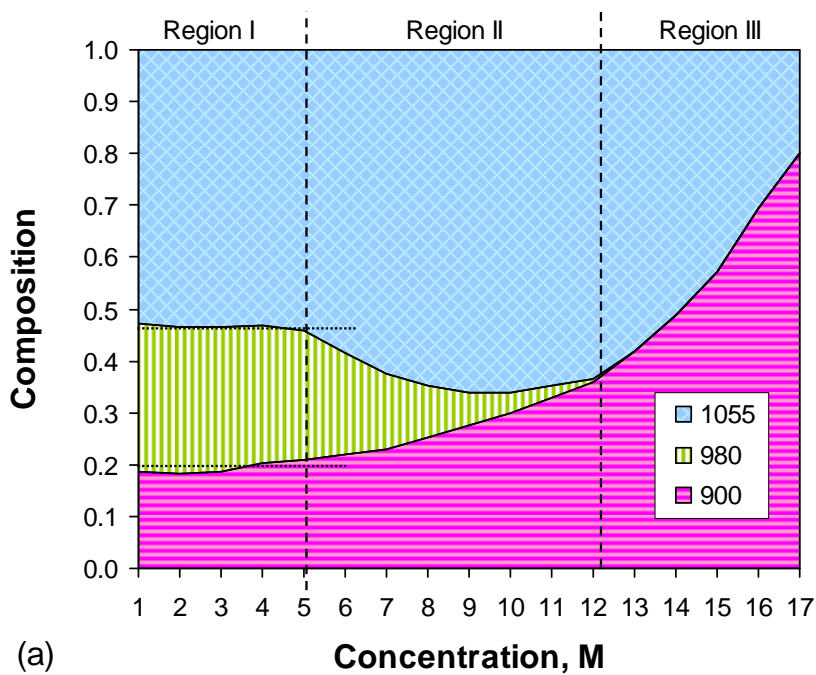


Fig. 3. Composition-concentration diagram for the main Raman scattering bands of aqueous sulfuric acid. (a) Results of the present study. Horizontal dotted lines represent “idealized” constant composition below ~5 M. Area fluctuations at lower concentrations are not considered significant and may result from technical/experimental artifacts. (b) Results of Rao⁹ used by Young and Blatz.⁸ The “horizontal line” lying at close to zero on the composition axis, between 0 and 6 M, and representing the 980 band, depicts measured values that are substantial but too small to show on the scale of this composition diagram. For consistency with (a), Rao’s results were extrapolated to 1 M, assuming no change in spectral behavior below 3 M.

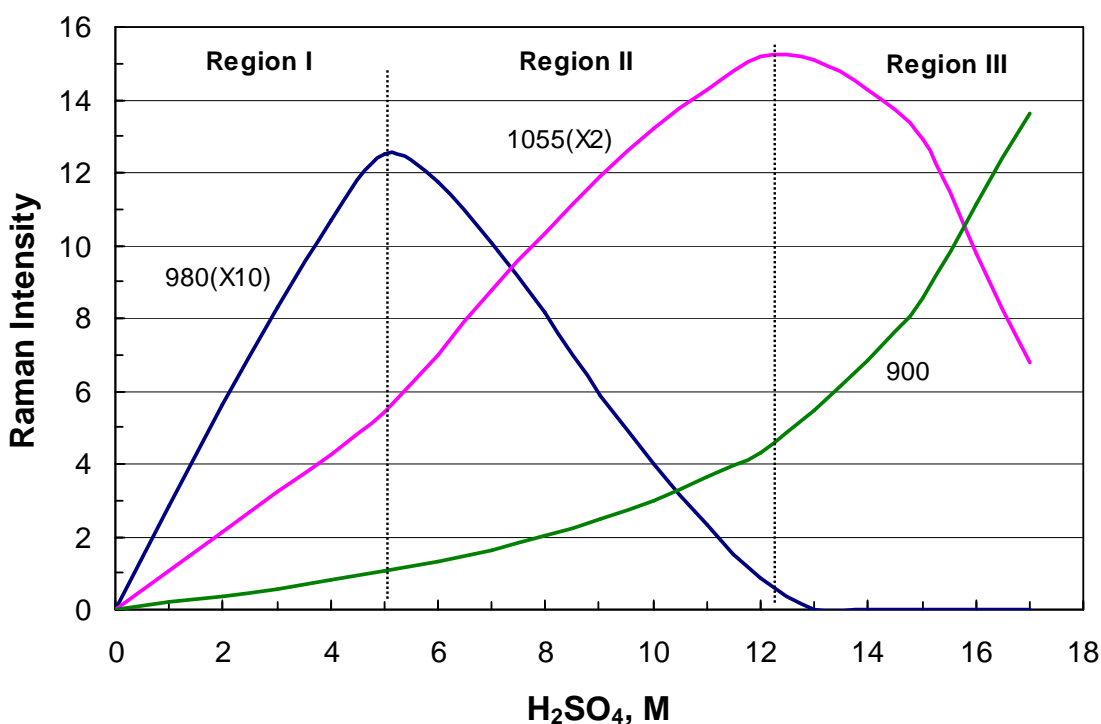


Fig. 4. Effect of acid concentration on the intensity, in arbitrary units, of the three major stretching vibration bands of the Raman spectra of aqueous sulfuric acid.

Interpretation of the Raman spectra of aqueous sulfuric acid. Based on the Raman scattering results as presented in Figs 1 – 4, one should conclude the following.

- (1) The spectra of aqueous sulfuric acid up to 12.5 M do not support, let alone prove, the notion that the acid is H_2SO_4 ; this is so since below 12.5 M the 1150 band, characteristic of H_2SO_4 (see below), is absent; the presence of H_2SO_4 is, however, indicated above 12.5 M and this acid appears to be best represented by the 16.8 M spectrum.
- (2) There is no evidence (*e.g.*, the 1150 band) for undissociated H_2SO_4 below ~5 M.
- (3) There is only one complete dissociation event above ~0.1 M, as indicated by the constant spectroscopic pattern up to about 5 M.
- (4) There is a clear transition of the Raman scattering pattern between ~5 M and ~12.5 M.
- (5) There is a further transition *of a different nature* above ~12.5 M.

The new Raman study is therefore indicative of a different structure of sulfuric acid in water than hitherto claimed, and a spectral pattern reflecting (a) a complete ionization of the acid up to about 5 M; (b) a gradual ion association, creating the free acid, between ~5 and ~12.5 M; and (c) additional structural changes of the fully associated acid above 12.5 M.

Key to contesting the traditional interpretation of the Raman scattering spectra of sulfuric acid in water, is the realization that each ionic and molecular species related to H_2SO_4 in water is not necessarily characterized by only one Raman band (see above); instead, a species may exhibit a pattern of one or more Raman shifts. Also, each band may probe more than one species (possibly, with a small frequency difference). It is quite

apparent that the acid is fully dissociated below ~5 M, essentially to a single anionic species; therefore, that anionic species has a spectral pattern comprising *all* three major stretching vibration modes (ν_{SOH} , ν_1 and ν_s). Also, between ~5 and ~12.5 M there is a gradual ion association to a free (molecular) acid that is characterized by only two of the three main modes of vibration – ν_{SOH} and ν_s . The “total symmetric stretching of SO_4^{2-} ” ν_1 , at 980 cm^{-1} , is thus characteristic of an anionic (electron charged) sulfur oxide species in the solution hence reflects $\text{O}=\text{S}-\text{O}^-$, or $(\text{O}^--\text{S}^+=\text{O})^-$, (i.e., “ SO_2^- ”) type ionic segments. The assumption⁸ that HSO_4^- remains a major ionic species at even 17 M is clearly inconsistent with the disappearance of the 980 band at and above ~13 M (Figures 3a, 4). Moreover, not only are the 1055 and 980 bands both characteristic of the HSO_4^- ion, but the 1055/980 peak ratio of this ion (in dissociated H_2SO_4 solution) is almost constant over orders of magnitude of concentration.¹⁹ Tomikawa and Kanno have claimed^{15a} that the 900 peak (ν_{SOH}) is also characteristic of HSO_4^- . They have further explained the disappearance of the 980 peak (ν_1) as indicative of the elimination of SO_4^{2-} ; yet – in strong disagreement with their interpretation – the latter ion is not believed in the literature^{6,7,10} to be present to a significant extent above ~0.1 M.

In view of the above, it is plausible that the bisulfate ion exhibits the three major bands (ν_{SOH} , ν_1 , and ν_s) because in its tetrahedral structural arrangement, having C_1 symmetry, this anion has S–OH, S–O⁻ and S=O bonds probed by the vibrating segments $(\text{O}^-)\text{--S--OH}$, $\text{O}=\text{S--O}^-$ [$\leftrightarrow (\text{O}^-)\text{--S}=\text{O} \equiv (\text{O}^--\text{S}^+=\text{O})^-$], and $\text{O}=\text{S--OH}$, respectively. The tetrahedral SO_4^{2-} , with T_d symmetry, has only one strong Raman shift, at 980 cm^{-1} (ν_1), since this ion possesses only S–O⁻'s as S–O single bonds that are probed in the Raman spectra by the $\text{O}=\text{S--O}^-$ vibration

segment (ν_1). Through resonance of its electronic structure, $\text{O}=\text{S}-\text{O}^-$ equalizes all four bonds in SO_4^{2-} , thereby creating the T_d symmetry and the strong intensity of its 980 Raman band. Since SO_4^{2-} is indeed missing at 1 – 5 M, what exists in this concentration range is a hydrosulfate; the literature claims that this is HSO_4^- , but this negates the fact that the aqueous acid behaves thermodynamically as a strong 1–3 electrolyte, not a strong 1–1 electrolyte.³

Correlation between vibrational spectral bands and the structure of aqueous species of sulfuric acid. Let us now try to reconcile the current Raman findings with the recently proposed structures of the acid and its anion.³ *Parasulfuric acid*, H_4SO_5 , with a pentacoordinate structure of a central sulfur atom surrounded by five oxygen atoms (one as “O” and four as “OH”), has been postulated^{3–5} as the acid in water; the aqueous acid has been proposed to fully dissociate in water according to $\text{H}_4\text{SO}_5 \rightarrow 3\text{H}^+ + \text{HSO}_5^{3-}$, so the trivalent *parabisulfate* ion, HSO_5^{3-} , is the only sulfur oxyhydroxide ion in solution. From Raman spectroscopy viewpoint, H_4SO_5 is not considerably different than H_2SO_4 : The two acids share similar bond types and they both possess the 900 and 1055 stretching vibration modes; also, being electrically neutral sulfur oxide species, they lack the 980 vibration mode that is typical to the ions in which at least one S–OH bond has been converted to a S–O[−] bond (see above). For similar reasons, HSO_5^{3-} is not readily distinguishable from HSO_4^- . However, one very significant Raman difference between H_2SO_4 and H_4SO_5 is the 1150 cm^{-1} band that exists only in the former acid structure since it arises from $\text{S}(=\text{O})_2$ (i.e., $\text{O}=\text{S}=\text{O}$) stretching.^{16,28} [Because of a resonance of the type $\text{O}=\text{S}^+=\text{O}^- \leftrightarrow (\text{O}^-)=\text{S}^+=\text{O}$ (or $\text{O}^{\delta-}=\text{S}^{\delta+}=\text{O}^{\delta+} \leftrightarrow \text{O}^{\delta+}=\text{S}^{\delta-}=\text{O}^{\delta-}$), such a vibrational mode is not seen in the tetrahedral sulfate ions.]

The constant 900–980–1055 pattern of aqueous sulfuric acid up to moderate concentration can thus be interpreted as that of the ionic species HSO_5^{3-} and not necessarily HSO_4^- . Further dissociation of the trivalent anion does not occur (except, perhaps, at extreme acid dilution) since the thermodynamic state of the SO_5^{4-} anion in aqueous solution is very unfavorable and the ion apparently cannot be effectively stabilized by hydration.²⁹ However, the initial relative higher intensity of the 980 band, as shown in Figure 1a, may indicate some SO_5^{4-} presence (and not the presence of SO_4^{2-} !) as a result of partial dissociation of HSO_5^{3-} at extremely dilute acid solutions.

Region I in Figures 3a and 4 is therefore that of full dissociation of H_4SO_5 . Above ~5 M, ion association starts to gradually take place within the concentration range of Region II, as indicated by the spectral transitions occurring in this region. As more S–OH bonds form at the expense of S–O⁻ bonds, the 1055 band (ν_s -SO₂H, i.e., ν_s of O=S–OH) increases and the 980 band (ν_1 -SO₂⁻, i.e., ν_1 of O=S–O⁻) decreases in intensity (Figure 4). At 12.5 M, the spectrum (Figure 1b) is most representative of H_4SO_5 , exhibiting the ν_{SOH} and ν_s modes but lacking the ν_1 mode. Region III marks a state of practically all-associated acids; initially, the most abundant neutral species is H_4SO_5 , with the highest population of S–OH bonds and lowest population of S:→O (or S=O) bonds; then, through dehydration (first, according to $\text{H}_4\text{SO}_5 \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$), H_2SO_4 , disulfuric (pyrosulfuric) acid, trisulfuric and even higher polysulfuric acids, and eventually – free sulfur trioxide, SO_3 – are all formed. In this acid dehydration process, there is a gradual loss of S–OH groups and creation of additional S:→O (or S=O) groups due to water elimination; in parallel, the symmetric vibrational mode (ν_s) of the 1055 band, after passing a maximum intensity and a maximum redshift (minimum in

frequency, see Figure 2b) – at ~12.5 M – declines in intensity and increases in frequency; the asymmetric mode ν_{SOH} (900 band), in contrast, exhibits a dramatic growth and a blueshift. This is attributable to an average increase in the S=O/S–OH ratio as concentration increases, so the observation of Young *et al.*^{8,10} that at ~18 M the 900 band passes a maximum is the result of a decrease in the S(OH)₂ population [S(OH)₂–to–S ratio] due to dehydrative polymerization of sulfuric acid.

Di- and polysulfuric acids have a new bonding type, S–O(–S), which I tentatively associate with the weak 970 vibration band seen above 15 M (Figure 1b). Also, the S=O bonds in those higher acids are probed by the 1150 stretching band [$\nu_{\text{s}}\text{-S(=O)}_2$] that develops in Region III and is primarily associated with H₂SO₄ (see above); likewise, the new very weak band at ~670 cm⁻¹ (Figure 1b) is apparently due to a bending vibration. The almost constant (~480 cm⁻¹) separation between the 1150 and 670 bands, the 1055 and 590 bands, and the 900 and 420 bands, suggests that these three sets of bands are stretching–bending vibration “couples” of the same types of atomic structural combination. In contrast with the other stretching vibration bands, the 980 band does not have a visible (*i.e.*, Raman-active) bending counterpart, which would have occurred at ~500 cm⁻¹.

Association of Raman scattering bands with sulfur-oxygen bonds. The above interpretation of the Raman spectra of aqueous sulfuric acid is based on the realization that – contrary to what has been claimed in the old literature – the stretching vibration bands do not probe entire ionic or molecular structures; instead, each band reflects a special stretching mechanism of a set of connected atoms (usually three) arranged in a certain fashion in a

molecular or ionic fragment. Even so, *these bands, in fact, probe specific bond types*. It is plausible that the 980 band probes and quantifies the S–O[−] ionic bond in its various states, and the 900 and 1055 bands similarly probe and quantify the S–OH bond; however, the 1055 band also probes the S=O bond. The 1150 band, occurring at very high acid concentration (see above), exclusively represents the S=O bond but only when the sulfur atom is doubly bonded to another oxygen atom, forming the molecular segment O=S=O. If only HSO₅^{3−} and/or H₄SO₅ and/or H₂SO₄ exist in solution as sulfur oxide species, then the 980 band (ν_1 -SO₂[−]) should reflect HSO₅^{3−} exclusively. The linear increase of this band with concentration up to 5 M is then the direct consequence of the addition of more HSO₅^{3−} to the solution when adding more acid, since in the 0 – 5 M region the ionization of H₄SO₅ is always complete. However, in this region the 900 and 1055 bands also probe only HSO₅^{3−} because other species exhibiting these bands (see above) are absent.

If between 5 and 12.5 M (Region II) ion association gradually converts HSO₅^{3−} to H₄SO₅, then one should expect the 980 band (ν_1 -SO₂[−]; S–O[−] bond) to decrease and the 1055 band (ν_s -SO₂H; S–OH bond) to increase with concentration; *this indeed happens*. The rise of the 1055 band is because in Region II S–O[−] bonds convert to S–OH bonds and thus, the S–OH bond population increases in the “averaged species” in solution; over the entire Region II, the ratio S–OH/S varies with concentration from 1 to 4. Since in Regions I and II there is no change in the number of S=O bonds per average solute species (so the S=O/S ratio is constant), the density of these bonds increases only with increase in sulfate concentration; the growth of the 900 band [*i.e.*, ν_{SOH} , or ν_a -(SO₂H)[−] (at ~890 cm^{−1}); or ν_s -SO₂H₂ (at ~910 cm^{−1})] is moderate and about constant, and it is not linear with acid concentration.

According to the present interpretation of the Raman spectra, at the end of Region I HSO_5^{3-} reaches maximum concentration and it is almost the exclusive sulfate species in solution; therefore, Region I as a whole is that of ionization of the free acid. The end of Region II corresponds to almost only H_4SO_5 in the solution, and, therefore, Region II is that of ion association. The monotonic non-linear increase in the 900 band in Region II most probably arises from the stronger intensity of this band in H_4SO_5 (as the 910 cm^{-1} stretch) than in HSO_5^{3-} (as the 890 cm^{-1} stretch). In Region III, the 1055 band decreases, in accord with the elimination of S–OH bonds and creation of more S=O bonds due to successive acid dehydration steps (first converting H_4SO_5 to H_2SO_4). The 900 band increases more strongly in Region III than in Region II (Figures 3a and 4) because $\nu_s\text{-SO}_2\text{H}_2$ (at $\sim 910\text{ cm}^{-1}$) is stronger in H_2SO_4 than in H_4SO_5 . Region III is, thus, that of molecular acid dehydration.

Summary: Raman scattering of aqueous sulfuric acid and its variation with acid concentration – $\text{HSO}_4^-/\text{H}_2\text{SO}_4$ versus $\text{HSO}_5^{3-}/\text{H}_4\text{SO}_5$. It seems that no other interpretation of the Raman spectrum of aqueous H_2SO_4 can be as coherent as the one offered here. If the acid is a 1–1 strong electrolyte H_2SO_4 , ionizing to practically only HSO_4^- as sulfate ion, then the Raman behavior may be explained in a manner parallel to the above, with HSO_4^- replacing HSO_5^{3-} and H_2SO_4 replacing H_4SO_5 . But, as argued before, the acid should be completely ionized up to 5 M, gradually associating between 5 and 12.5 M, then undergoing dehydration above 12.5 M. H_2SO_4 dehydrates first to disulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$. If acid dissociation in solution is represented by the equation $\text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^-$, then this contrasts with the 1–3 electrolyte behavior of the aqueous acid. But in addition, if what forms at 12.5 M is H_2SO_4

and not H_4SO_5 , where is the 1150 cm^{-1} band? Why does this band appear only at 15 M and higher concentration? It is also implausible that significant dehydration of H_2SO_4 to $\text{H}_2\text{S}_2\text{O}_7$ would occur at the concentration range of Region III (*i.e.*, below 17 M).

The Raman spectral interpretation of aqueous sulfuric acid, as offered in the present article, is summarized in Table 1 as stretching vibration types, and in Table 2 as specific frequencies of the different main stretching bands of the various sulfur oxide ions and molecules relevant to the acid in water.

Table 1 Structure assignment of Raman scattering stretching vibrations of aqueous H₂SO₄: Old vs. new

band ^a	old assignment	new assignment ^b	type ^b	current structure ^c	proposed structure ^c	comments ^d
900 cm ⁻¹	H ₂ SO ₄	ν_{SOH}	asymmetric	OH-S-O ⁻ (890); HO-S-OH (910)	HSO ₅ ³⁻ , H ₄ SO ₅ , H ₂ SO ₄ , higher acids	A
980 cm ⁻¹	SO ₄ ²⁻	ν_1	total symmetric	O=S-O ⁻	HSO ₅ ³⁻	B
1055 cm ⁻¹	HSO ₄ ⁻	ν_s	symmetric	O=S-OH	HSO ₅ ³⁻ , H ₄ SO ₅ , H ₂ SO ₄	C
1150 cm ⁻¹	H ₂ SO ₄ ^e	ν_s	symmetric	O=S=O ^e	H ₂ SO ₄	D

^a approximate location.

^b ref 15.

^c according to the present work, a scattering band probes/quantifies the mentioned bond type, see text; proposed atomic segments active in the stretching vibration modes are of the type S-OH(OH) and S-OH(O⁻) for ν_{SOH} , S-O⁻(=O) for ν_1 , S-OH(=O) for ν_s -SO₂H, and S=O(=O) for ν_s -SO₂.

^d A – band intensity increases with concentration during dissociation, and more steeply during acid dehydration. B – band intensity increases with concentration at full dissociation, and decreases during ion association; band missing during acid dehydration. C – band intensity increases with concentration at full dissociation and during ion association, and decreases during acid dehydration. D – band forms at and above 15 M.

^e ref 28.

Table 2 Values of Raman shifts (in cm^{-1}) of the various stretching vibrations of different possible species in aqueous sulfuric acid^a

species ^b	$\nu_{\text{s}}\text{-S(OH)}_2$	$\nu_{\text{a}}\text{-S(OH)O}^-$	$\nu_{\text{s}}\text{-S(=O)O}^-$	$\nu_{\text{s}}\text{-S(=O)OH}$	$\nu_{\text{s}}\text{-S(=O)}_2$
SO_4^{2-}	--	--	982 vs	--	--
HSO_4^-	--	885 w	980 s	1047 vs	(1192 w)
HSO_5^{3-}	--	900 w	987 s	1050 s	--
H_4SO_5	908 s	--	--	1037 s	--
H_2SO_4	917 vs	--	--	1050 w	1150 w

^a w – weak, s – strong, vs – very strong; in parentheses, suspected band.

^b for SO_4^{2-} and HSO_4^- , according to the literature, *e.g.*, ref 14; see text.

Physicochemical viability of pentacoordinate sulfur oxide

Structural and chemical considerations. Suggesting a molecular sulfur oxide type acid that is not based on a tetrahedral geometry around the central sulfur atom appears unprecedented; no published work prior to my three recent articles³⁻⁵ seems to have advanced the idea that a pentacoordinate sulfate molecule or ion may exist in solution. The tetrahedral H_2SO_4 structure is a result of a 3→4 coordination expansion in the planar trigonal SO_3 molecule¹⁸ (with D_{3h} symmetry) due to its chemical reaction with a H_2O molecule *via* the splitting of this molecule to form two coordinating OH groups on the central S atom. H_2SO_4 is sometimes referred to as sulfur trioxide hydrate, or $\text{SO}_3 \cdot \text{H}_2\text{O}$, and many other hydrates of SO_3 are known,^{19,20} among them $\text{SO}_3 \cdot 2\text{H}_2\text{O}$ (or $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$). However, there is no suggestion in the literature that this well-known sulfur trioxide dihydrate (see below) may have the two hydrating H_2O molecules on the SO_3 split, thus forming – through a 3→4 coordination expansion of SO_3 , followed by 4→5 coordination expansion of H_2SO_4 – the pentacoordinate H_4SO_5 [or $\text{SO}(\text{OH})_4$]. A H_5SO_5^+ ion was once considered by Young and Walrafen²⁵ but later dismissed by Walrafen.²⁶ Even so, that proposed species was still based on a tetrahedral sulfate, and was believed to be a sulfuric acid “solvated” hydronium ion, $\text{H}_2\text{SO}_4 \cdot \text{H}_3\text{O}^+$. An ion-pair $\text{HSO}_4^- \cdot \text{H}_3\text{O}^+$ (formally H_4SO_5 , but a tetrahedral sulfate structure) was proposed by Chen and Irish,²⁴ based on Raman studies, and it was associated with the interrelation between half-widths of the 980 and 1055 cm^{-1} Raman bands.²⁷

“ H_4SO_5 ” – or $\text{SO}_3 \cdot 2\text{H}_2\text{O}$ as it is referred to in the literature –exists in the phase diagram of the SO_3 – H_2O system as a stable molecular species,^{19,21} forming a peak at ~69% wt SO_3

(“85% H₂SO₄”) with a melting point of 8.62 °C. It is plausible that the preferred structure of aqueous sulfuric acid up to 85% wt H₂SO₄ (15.4 M) is H₄SO₅ and not H₂SO₄. Yet, salts of the acid, whether in solution or in their pure solid state, could be mostly, or exclusively, those of the tetrahedral HSO₄⁻ and SO₄²⁻ ions,⁴ since these ions may be more stable than the pentacoordinate sulfate ions, at higher pH and higher concentration. Thus, when the acid is neutralized, the Me⁺-2H⁺-HSO₅³⁻ system (Me = Na, K, etc.) may initially be stable, but then, as concentration increases, this system may disintegrate to form the bisulfate ion through water elimination causing 5→4 coordination contraction of the pentacoordinate sulfate structure. The 2Me⁺-H⁺-HSO₅³⁻ system could similarly undergo water elimination to the more stable 2Me⁺-SO₄²⁻ system; or, SO₄²⁻ may be formed by base neutralization of HSO₄⁻.⁴

Sulfuric acid in water as a completely dissociated electrolyte. In the mid-1920s, Noyes published a series of articles on “The Inter-Ionic Attraction Theory of Ionized Solutes” in which he developed methods for the derivation of ionization constants of weak or mild electrolytes based on the theory of Milner and that of Debye and Hückel. In Part VI of that series, Sherrill and Noyes devoted a considerable effort to the study of the ionization of the bisulfate anion.³⁰ Many have followed this pioneering work in interpreting the behavior of sulfuric acid in aqueous solution as a partly dissociated electrolyte^{6,7,31,32} to explain the change of the activity coefficient and the osmotic coefficient of the acid as a function of concentration. In Part I of his article series,³³ Noyes wrote: “*Evidently, in case this theory [of Debye and Hückel] proves to account fully for the deviations of the behavior of ions from that of perfect solutes, it will confirm the view, recently supported by several investigators*

[references cited] *that most of the largely ionized substances are practically completely ionized up to moderate concentrations.*” The evidence, based on the Debye–Hückel (DH) limiting law and on DH–SiS,³ that sulfuric acid in water behaves as a 1–3 electrolyte completely dissociated to ions up to ~5 M, is derived from the ionic activity of the acid and its response to the variation in acid concentration; this behavior strictly follows that of typical strong 1–3 electrolytes, such as $\text{K}_3\text{Fe}(\text{CN})_6$.³ Furthermore, γ_{\pm} values of the acid at very low molality (m) strongly suggest an asymptotic approach to the 1–3 line of the DH limiting law.³ In contrast, aqueous Li_2SO_4 (a proven strong 1–2 electrolyte³) differs considerably from aqueous H_2SO_4 in terms of γ_{\pm} at any given concentration: γ_{\pm} of Li_2SO_4 is always much higher than that of the acid, implying a far stronger electrostatic attraction in the acid solution than attainable with any solution of a strong 1–2 sulfate electrolyte.³

Concentration effect on the freezing point of aqueous sulfuric acid, and its correlation with Raman shifts. Also indicative of a fully dissociated 1–3 acid up to ~5 M, is the unusual dependence of the freezing point and the electric conductivity of aqueous H_2SO_4 on acid concentration. The known maximum in electric conductivity (and minimum in specific resistivity²²) at ~32% wt H_2SO_4 (~4 M) should occur at maximum ionic concentration, and so is the minimum in the freezing point curve²¹ (at about -72 °C); indeed, down to this lowest freezing temperature, occurring at 4.9 M, the solution freezes as pure ice,²¹ reflecting full acid ionization (*i.e.*, no electrically neutral molecular sulfur oxide structure present). These anomalous physical characteristics thus tend to corroborate the findings and conclusions of the current study. It is, therefore, pleasing to reveal that such properties correlate with the

Raman spectral behavior of the aqueous acid (see above) in a manner not recognized hitherto. This is shown in Figure 5 in which the freezing point curve of aqueous H_2SO_4 is plotted against acid molar concentration, and in parallel, products of Raman stretching band intensities are also plotted. Up to the first freezing point minimum, at ~ 5 M, where the solution freezes as pure ice, we have Region I of the above Raman analysis (Figures 3a and 4), in which the acid is fully ionized. No sulfate species freezes out from the solution in this region (0 – 5 M) since all the sulfate is in an anionic state. Also, the strong initial decrease in the freezing point curve is evidently the result of the increasing concentration of the trivalent anion HSO_5^{3-} and the accompanying protons that are three times more concentrated than if the acid dissociated as a 1–1 electrolyte. In parallel, in Region I, the product of the 980 and 1055 bands steadily increases, as a mirror image of the freezing point depression.

The borders between the three concentration regions as presented and discussed above, that is, the two vertical dotted lines in Figure 5 (as in Figures 2c, 3a and 4), coincide with the two dips in the freezing point curve and these dips thus mark the onsets of forming H_4SO_5 by ion association (5 M dip) and H_2SO_4 by dehydration of H_4SO_5 (~ 12 M dip). The two freezing point minima occur, respectively, where the maxima of the 980 and 1055 band intensities occur (Figure 4). Plotting the product of the intensities of the 980 and 1055 bands is done to locate the approximate equimolar point of HSO_5^{3-} and H_4SO_5 in Region II (ion association), as the maximum of the curve. This 980 \times 1055 maximum is somewhat below the first local maximum in the freezing point curve, which could be an artifact due to some small inaccuracies in the analysis of the Raman data; so possibly, the equimolar ion–acid point is better probed by the freezing point maximum (at ~ 8.5 M). The maximum in the curve of the

product of the intensities of the 900 and 1055 bands is interpreted as the equimolar point of the $\text{H}_4\text{SO}_5\text{-H}_2\text{SO}_4$ split in Region III. This maximum coincides with the second maximum in the freezing point curve, at ~ 15 M. The pattern of the freezing point curve above the first minimum (5 M) is not well understood yet but it has been claimed²¹ to correspond to preferential formation, upon freezing, of various distinct sulfuric acid hydrates.

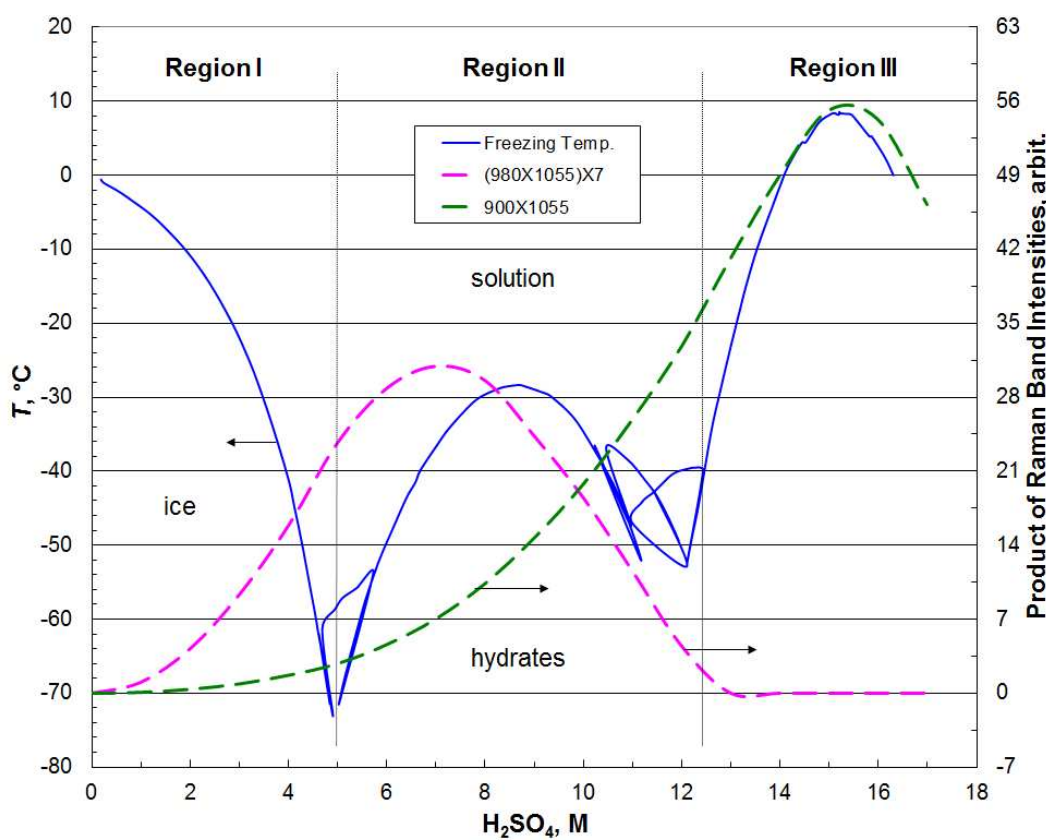


Fig. 5. Correspondence of the freezing point curve of aqueous sulfuric acid as a function of concentration (blue full line, left axis; data from Table 1 of ref 21), and Raman band intensity curves (dashed lines, right axis, arbitrary unit; this work): The red dashed line is the 980 band intensity multiplied by the 1055 band intensity ($\times 7$); the green dashed line is the 900 band intensity multiplied by the 1055 band intensity. See text for explanation.

The comparison in Figure 5 is compelling even if not yet fully explainable. It is less likely that the ion causing the strong freezing point drop in Region I is HSO_4^- ; as a univalent anion, like Cl^- and NO_3^- , produced by acid dissociation along with only one H_3O^+ ion per acid molecule, HSO_4^- would cause a milder freezing point drop, similar to that of the 1–1 strong electrolyte acids HCl and HNO_3 . The dissociation of H_4SO_5 , giving three hydronium ions per acid molecule, creates an ionic state that prevents freezing more effectively and it also causes higher electric conductivity (and less electric resistivity).

Related to the above are sulfuric acid aerosols in the troposphere and stratosphere, which are formed due to sulfur-borne atmospheric pollution. In view of the considerable attention given nowadays to climate changes and the possible role of sulfuric acid aerosols in such changes – for example, in polar stratospheric clouds (PSCs)³⁴ – it is tempting to interpret the fact that such aerosols do not freeze at the tropopause (at and below $-55\text{ }^\circ\text{C}$) as resulting from the acid being a 1–3 electrolyte and the anionic species in the aerosol being HSO_5^{3-} electrically compensated by three protons (as H_3O^+ ions), at concentration within the range $\sim 4 - 6\text{ M}$. However, PSCs with 50% acid (7 M) and even 75% acid (12.8 M) are also claimed to exist,³⁵ not freezing (and undergoing sedimentation) even at about $-100\text{ }^\circ\text{C}$. According to the present study, the aerosol particles in such PSCs mostly comprise $\text{HSO}_5^{3-}/\text{H}_4\text{SO}_5$ combinations within Region II (“ion association”) as defined above, and thus, not contain H_2SO_4 at all. At lower concentration, $<5\text{ M}$, sulfuric acid aerosols exclusively contain HSO_5^{3-} , not HSO_4^- and SO_4^{2-} as claimed in the literature. The increase in stratospheric moisture due to sulfur-borne pollution is evidenced nowadays, being regularly measured and monitored. The major factor responsible for this moisture increase is apparently the presence

of H_4SO_5 and HSO_5^{3-} in stratospheric aerosol, which prevents cloud sedimentation at low temperature.

Correlation of the Raman spectra and the apparent molal volume of aqueous sulfuric acid. In analyzing the apparent molal volume (ϕ_v) of sulfuric acid in water,³ I have demonstrated that in spite of the literature arguing otherwise, sulfuric acid does not seem to behave differently than other electrolytes at very low concentration; its ϕ_v does not indeed deviate from linearity with $C^{1/2}$ (“Masson rule”). I also concluded that even though one cannot distinguish between dissociation patterns of sulfuric acid solely based on ϕ_v and its variation with acid concentration, the experimental evidence is in very good agreement with a complete single-type acid dissociation within the concentration range of the ϕ_v measurements (0 – 3 M). In the analysis of ϕ_v , I have shown that the change of water density, $\Delta\sigma$, as the acid is being added, is proportional to the product of ϕ_v and C (molar concentration). In Figure 6, this density difference ($\Delta\sigma$),³ which is linear with concentration (Figure 8 in ref 3), is plotted against the sum of intensities of the 900, 980 and 1055 Raman scattering bands, at the same concentration values. Being the major Raman bands in the entire spectra of aqueous sulfuric acid, these three bands adequately probe the sum of concentration of all acid sulfate species in solution.

As anticipated, a linear behavior is clearly observed in Figure 6 in the 0.05 – 7.5 M concentration range. The sum of Raman intensities in the range of 0 – 5 M quantifies the amount of the anion of aqueous sulfuric acid. Since the anion is exclusively HSO_5^{3-} , the amount of this ion in solution is probed by both ϕ_v and the sum of intensities of the three

main Raman stretching vibration bands (or the intensity of each band). Thus, an internal consistency exists between the previously published analysis of the apparent molal volume of aqueous sulfuric acid,³ and the current analysis of the Raman scattering spectra of the acid.

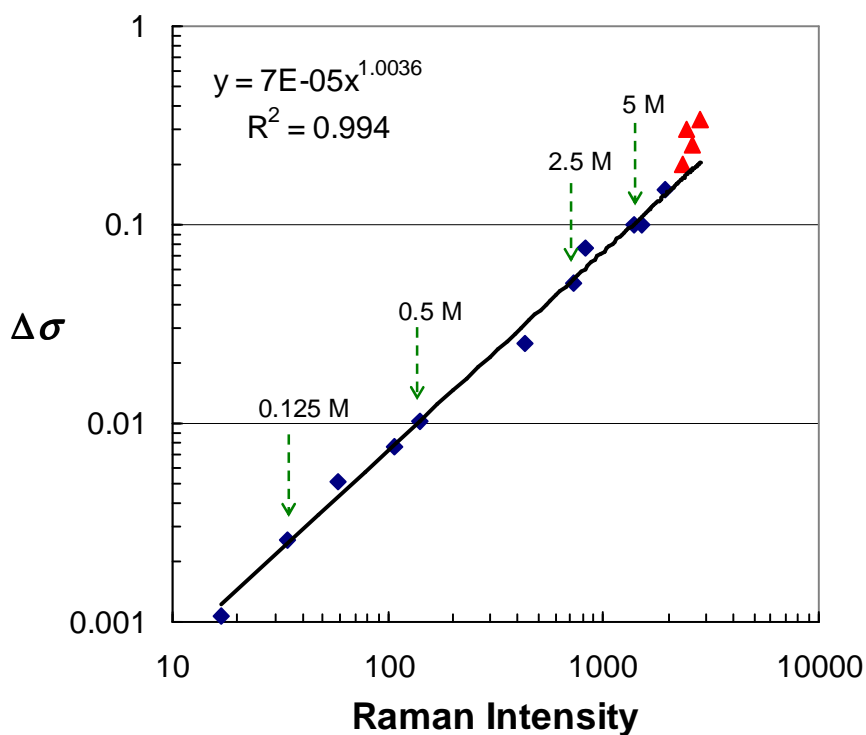
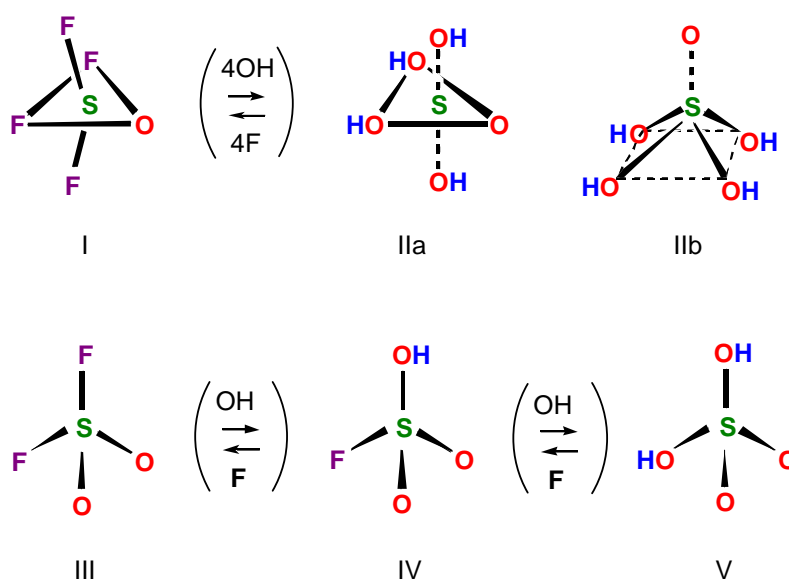


Fig. 6. Correspondence of $\Delta\sigma$ (water density difference, see text) of aqueous sulfuric acid solutions³ and the sum of intensities (in arbitrary unit) of the Raman scattering bands at 900, 980 and 1055 cm^{-1} , at the same concentration; a few concentration values are mentioned. The different symbols distinguish the main range of apparent linearity of $\Delta\sigma$ with total Raman shift intensity, from the non-linear range above ~ 7.5 M.

Analogy of H_4SO_5 and HSO_5^{3-} to related compounds and ions. In comparison with other sulfur oxide structures of the “ SO_5 ” type, H_4SO_5 is different in having all five oxygen atoms bonded directly to the central sulfur atom, with four S–OH bonds that are not necessarily

identical, and one S:→O (or “S=O”) bond. The proposed structure is thus reminiscent of the well-known structure³⁶ of SOF₄, in which a S=O bond (1.409 Å) is at one of the three corners of the triangle of a somewhat distorted trigonal bipyramid with the S atom at its center.¹ In view of the analogy between OH⁻ and F⁻ [e.g., compare H₂SO₄, or “(OH)SO₃H”, with fluorosulfuric acid, FSO₃H], it is plausible that a parallel structure exists with all F atoms of SOF₄ replaced by OH groups. This is illustrated in Scheme 1. A similar structure of pentacoordinate sulfate (“SO₅”) has been proposed by White *et al.*³⁷ for the surface sulfate group in sulfated zirconia, and the analogy to SOF₄ was drawn based on the similar infrared absorption band at ~1380 cm⁻¹, due to the S=O stretching vibration that exists in both structures.



Scheme 1 Analogy between hydroxy-sulfoxide and fluoro-sulfoxide structures: I, thionyl tetrafluoride; II, postulated *parasulfuric acid* (IIa in trigonal bipyramid structure; IIb in tetragonal pyramid structure; bold broken lines indicate bonds of uncertain exact geometry, regular broken lines in IIb emphasize that oxygen atoms of the four OH groups are expected

to occupy the corners of the tetragonal pyramid square base); III, sulfuryl difluoride; IV, fluorosulfuric acid; V, sulfuric acid.

The chemical viability of a pentacoordinate “SO₅”-based molecular structure draws further support from the straightforward analogy in the highest stable oxide forms of elements of the third row of the Periodic Table of the Elements, that is, as species of gradually decreasing oxidation number, going from atomic number 11 (Na) to 17 (Cl). This is demonstrated in Figure 7. The oxide can be represented initially by the EO_n^{1-n} formula, where E is the element and n , the maximum integer number of oxygen atoms bonding to E , going from 0 to 7. The initial bonding state is of ionic lattice, and later, of covalent bonding, as the character of E changes gradually from metallic to non-metallic; in parallel, E becomes more electronegative and it forms a smaller $E^{(n+1)+}$ cation of higher formal (*i.e.*, $n+1$) positive charge. The analogy is perfect up to E_{15} , that is, P: NaO_0^{1+} (= Na^+), MgO_1^0 (= MgO), AlO_2^{1-} , SiO_3^{2-} , PO_4^{3-} . However, it breaks down for the higher E 's S and Cl. For S, the analogy predicts a pentacoordinate SO_5^{4-} , and for Cl, a hexacoordinate (octahedral) ClO_6^{5-} . Instead, in reality the highest oxides are the tetrahedral SO_4^{2-} and ClO_4^- . This regressive trend, disrupting the above order, is explainable by the instability of hyperoxide structures with too small and too electronegative E 's. But going down the respective columns, the E 's (of row four, row five, etc.) become larger, less electronegative and of more metallic character.

It is well-known that the chemistry of selenium is similar to that of sulfur, and the chemistry of bromine is similar to that of chlorine;¹ in each of these element couples, the two elements have almost the same electronegativity. However, the chemistries of tellurium and iodine are quite different from those of the lighter elements in their column. Indeed,

paraperiodic acid, H_5IO_6 does exist – an analogue of the hypothetical H_5ClO_6 and H_5BrO_6 acids. H_5IO_6 has been isolated as pure compound, and the anion of its second ionization, $\text{H}_3\text{IO}_6^{2-}$ is also known as a stable structure.¹ The octahedral positions around the central I atom in the acid are occupied by five OH groups (I–O bond length, 1.89 Å) and one O (I=O bond length, 1.78 Å). H_5IO_6 is, however, a very weak acid with the constants of first three ionization steps separated by three orders of magnitude or more, and the first ionization constant being 5.1×10^{-4} . In the case of tellurium, the octahedral structure (of *orthotelluric* acid) H_6TeO_6 [or $(\text{HO})_6\text{Te}$] is known¹ and, in analogy to the sulfur case, it can be formally considered as tellurium trioxide trihydrate, $\text{TeO}_3 \cdot 3\text{H}_2\text{O}$. The dihydrate $\text{TeO}_3 \cdot 2\text{H}_2\text{O}$ (or H_4TeO_5) does not appear to have been ever reported, but its ion (conjugate base) due to complete ionization, that is, TeO_5^{4-} – with a trigonal bipyramid geometry – is known in salts,¹ such as $\text{Rb}_6[\text{TeO}_5][\text{TeO}_4]$. Thus, even though SO_5^{4-} may not be a stable sulfate anion, the hydroxy anion HSO_5^{3-} , in which the negative charge is somewhat relieved, may be a structure of borderline stability (metastability) between (the unstable) SO_5^{4-} and (the stable) SO_4^{2-} and HSO_4^- .

It therefore seems overall plausible, based on the above discussion, that the structure and dissociation pattern of aqueous sulfuric acid (and, in analogy, probably also that of aqueous selenic acid) is as recently proposed^{3–5} and as found in this article to be in accord with the Raman scattering shifts of the acid in water. I speculate that solvent effects (dipoles, permittivity, etc.) stabilize the pentacoordination of SO_5 , and high acidity destabilizes the tetrahedral sulfate structures.

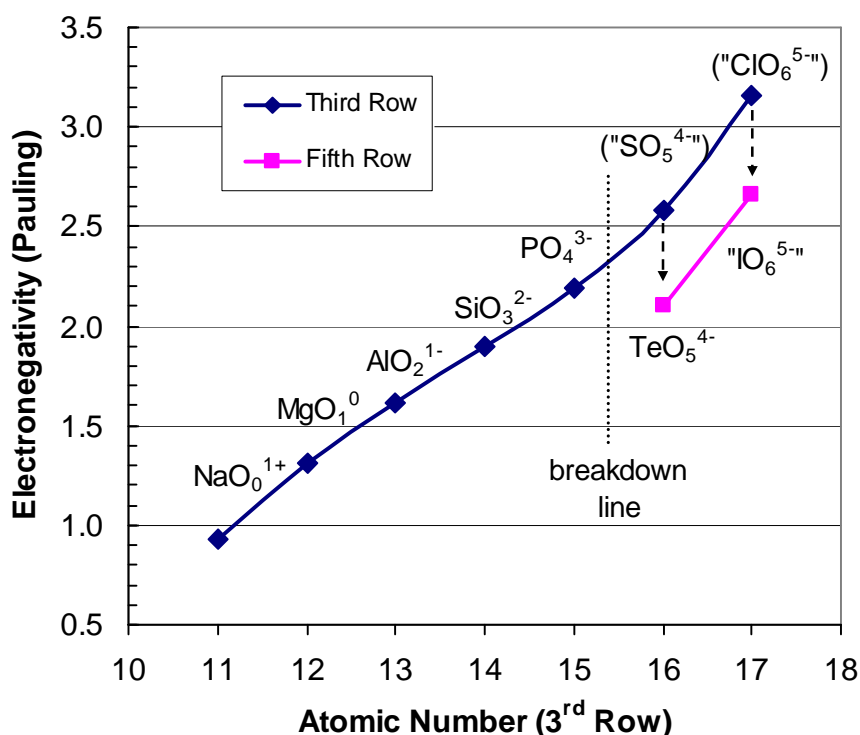


Fig. 7. Correlation between highest oxides of elements, presented on an electronegativity – atomic-number scale (quotation marks indicate ionic structure that could exist; quotation marks inside parentheses denote hypothetical oxo anion).

Conclusions

Raman scattering bands of aqueous sulfuric acid in the stretching vibration region are interpreted as fully supporting the existence of *parasulfuric acid*, H₄SO₅, as well as the trivalent *parabisulfate* ion, HSO₅³⁻. While the HSO₅³⁻/H₄SO₅ pair cannot be unambiguously distinguished from the parallel HSO₄⁻/H₂SO₄ pair based on the spectral analysis, the pattern of spectral changes with acid concentration prefers the former ion–acid set. Strongly supporting the presence of H₄SO₅ over H₂SO₄ in the ion association region (Region II, 5 –

12.5 M), is the absence of the ν_s -SO₂ vibrational band at 1150 cm⁻¹, which is characteristic of H₂SO₄ but not of H₄SO₅; this band appears only at and above 15 M. According to the current study, there is no unequivocal evidence, based on Raman spectra, for the traditional view of the structure and ionization of aqueous H₂SO₄.

The strong decrease in freezing point of the acid–water system at increasing acid concentration, down to –72 °C at ~5 M, and the unusually high electric conductivity of acid solutions of parallel concentration (as measured at 25 °C), although well-known, are two curious physical features of aqueous sulfuric acid contrasting with the parallel properties of simple 1–1 mineral acids. This may be due to the fact that aqueous H₂SO₄ is not a strong 1–1 electrolyte (above 0.1 M) but, instead, a strong 1–3 electrolyte. Moreover, I have now demonstrated a compelling parallel, hitherto unknown, between the anomalous freezing point behavior and the Raman spectroscopic pattern of aqueous sulfuric acid. The proposed 1–3 acid, H₄SO₅ (≡ “SO(OH)₄”), is structurally analogous to the well-known stable compound thionyl tetrafluoride, SOF₄.

The present investigation indicates, as before,^{3–5} that the literature has so far mischaracterized aqueous sulfuric acid in terms of its chemical structure and molecular and ionic speciation. Simple thermodynamic evidence, based on the response of γ_{\pm} of the aqueous acid to the change in acid concentration (m), according to which the acid behaves as a typical strong (fully dissociated) 1–3 electrolyte,³ precludes the possibility that H₂SO₄ in water dissociates to either HSO₄⁻ or SO₄²⁻. The new interpretation of the Raman spectra of aqueous sulfuric acid, provided in this paper, strongly suggests that in the concentration range of approximately 5 – 12.5 M, the acid is H₄SO₅ – *parasulfuric acid*; at higher concentration, this

acid dehydrates to H_2SO_4 , and at lower concentration, 0 – 5 M, it completely dissociates to three H^+ ions and the trivalent HSO_5^{3-} (*parabisulfate*) anion. If indeed H_4SO_5 and HSO_5^{3-} – not H_2SO_4 , HSO_4^- and SO_4^{2-} – are the prevailing molecular and ionic sulfate species formed in aqueous solution of sulfuric acid, then they are the first two cases of a distinct and thermodynamically stable chemical structure, at the molecular level, exhibiting pentacoordination of five oxygen atoms to a central sulfur atom.

The anomaly of aqueous sulfuric acid (e.g., its unexpected freezing point depression at increasing concentration) has been known for many decades, and the fact that the acid solution clearly follows the pattern of strong 1–3 electrolytes rather than being a partly-weak 1–1/1–2 electrolyte, should have been noticed long ago. It is thus puzzling that the inevitable relation between the above facts and the structure and ion speciation of H_2SO_4 in water has never been given serious consideration in the standard literature, including the most authoritative monographs on electrolyte solutions,^{6,7} and major textbooks of physical chemistry.^{38–40}

Acknowledgments

This study is based in part upon work supported by the U.S. Department of Energy under award Number DE-FG02-07ER84879. I am indebted to Mr. Christopher A. Starr for skillfully assisting in the Raman scattering experiments and their raw data processing. Thanks are also due to Professor Moshe Levy and Professor Guy C. Berry for critical comments and suggestions during the process of composing this paper.

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why the ν_1 band intensity increases as temperature decreases (refs 15 and 17); this
provides an alternate interpretation of the low temperature effect to that of the
literature. According to the literature, the HSO_4^- dissociation increases with
decreasing temperature, but this is counterintuitive. A plausible explanation for the ν_1
intensity increase at lower temperature is geometric (bond angle) changes in the
pentacoordinate *parabisulfate* ion, *e.g.*, if at lower temperature the tetragonal pyramid
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Structure and ionization of sulfuric acid in water

High-sensitivity Raman spectra of aqueous H_2SO_4 indicate that the acid in water is H_4SO_5 dissociating to $3\text{H}_3\text{O}^+$ and 1HSO_5^{3-} .

