The Study of the Raman Band Shape of Sulfuric Acid and Proton Transfer

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The Raman bands of sulfuric acid and ammonium sulfate in aqueous solutions were observed in the S–O stretching region and were resolved into components with a Voigt profile. The concentration dependence of the half band-widths was examined. The 980 cm^{-1} band of SO_4^{2-} in acidic solutions was determined to have a width of 8.0 ± 0.3 cm^{-1} when unbroadened by any chemical process. In the concentration-half-width curve for this band, two conspicuous bends were found, at about 2 M and 8 M stoichiometric concentrations of H_2SO_4. It seems that the former bend is attributable to the disappearance of water clusters, and the latter, to the partial defect of the primary hydration shell of the oxonium ion. The interrelation between the half-widths of the 980 cm^{-1} and 1050 cm^{-1} bands suggests that the formation of the $HSO_4^- \cdot H_3O^+$ ion pair is related to the spectroscopic lifetime of HSO_4^-.

It has been pointed out that the half-width of a Raman line of an anion, A^-, in acidic solutions yields the lifetime of A^-, which is determined by the rate of proton transfer between the A^- and H_3O^+ ions.[1,2] Chen and Irish reported, in their elaborate Raman spectral studies of hydrogensulfate–sulfate systems,[3,4] that the broadening of the 980 cm^{-1} line of SO_4^{2-} in acidic solutions is directly proportional to the oxonium ion concentration, $[H_3O^+]$, in the range lower than 2M, and that the proportionality changes abruptly at about $[H_3O^+]=2$ M. They evaluated the rate constant of proton transfer to be $5.5\times10^{11}M^{-1}s^{-1}$.

The resolution in these spectroscopic measurements was 10—15 cm^{-1}; such a low resolution might considerably affect the estimates of the band widths and the band shapes. The present study has been performed under a higher resolution in order to confirm or improve the previous results, or at least to gain some information.

Experimental

Solutions were prepared from H_2SO_4 (analytical reagent) and $(NH_4)_2SO_4$ (biochemical reagent) purchased from Wako Fine Chemicals. No impurity disturbing band analysis was detected from the observed spectra. The concentrations of sulfuric acid were determined from the specific gravity by referring to the standard table.[5] Raman lines excited by the 6328 Å line of a He–Ne gas laser were recorded on a JASCO R-300S Raman spectrophotometer at room temperature, 22 ± 2 °C. No temperature effect was appreciable on the observed spectra in this temperature range. Spectral slit widths were set at less than 2 cm^{-1} except for the 0.5 and 0.8 M sulfuric acid solutions, for which they were set at about 5 cm^{-1}.

Band Analysis

The observed spectral intensity, $I(\nu)=S(\nu)/(\nu-\nu_e)^4$, ranging from 850 to 1100 cm^{-1}, was resolved into components with the Voigt profile by the least-squares method, where $S(\nu)$ is the observed relative scattering intensity at a Raman shift of ν cm^{-1} and where ν_e is the wave number of the exciting line, 15803 cm^{-1}. The Voigt function is given by a convolution of the Lorentzian and Gaussian functions as follows:

$$V(\nu) = N\int_{-\infty}^{+\infty} \frac{\exp\left[-(\nu'/\beta_g)^2\right]}{(\nu-\nu')^2+\beta_l^2}d\nu' \quad (1)$$

Practically, however, an approximate representation for $V(\nu)$ given by Kielkopf[6] was used to calculate the numerical values of $V(\nu)$. Extraneous scattering light, probably the wing of the Rayleigh scattering, overlaps in this region. It forms a nearly straight background. The $S(\nu)$ was then determined by subtracting the background from the observed total scattering intensity.

The effect of the finite slit width on the band shape cannot necessarily be neglected for the relatively fine band of SO_4^{2-} at 980 cm^{-1}. A spectral slit function is well approximated by a Gaussian function.[7] Therefore, for the 980 cm^{-1} bands of the salt and the 0.5 and 0.8 M sulfuric acid solutions, β_g's were fixed at values given by $\beta_g=S/2\sqrt{\ln 2}$,[8] where S is the spectral slit width. The appropriateness of this processing is shown in Fig. 1 for the salt solution. Twice the best fit values of β_l were then adopted as the true half-widths. They were smaller by about 10% than the apparent half-widths; for example, the apparent half-widths of 13.3 and 15.4 cm^{-1} for 0.5 and 0.8 M sulfuric acid solutions were diminished to 11.4 and 13.8 cm^{-1} respectively. As a band broadens out and as a slit width becomes narrow, the effect of the finite slit width decreases rapidly. Thus, in the analyses of bands other than those mentioned above, the effect of the finite slit width was not taken into account and the half-width of the best-fit Voigt profile was adopted as that of each component band.

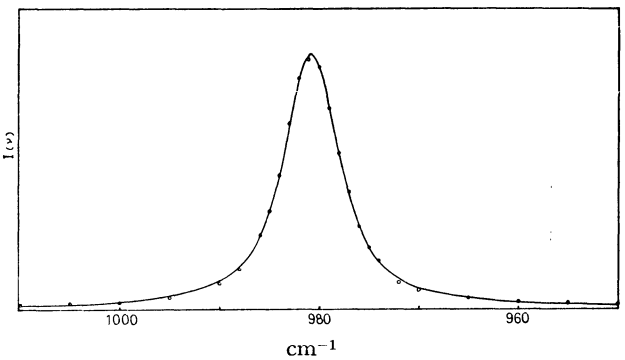

Fig. 1. Raman band of the 1.5 M ammonium sulfate solution.
° ° ° Observed intensity, —— calculated intensity with the Voigt profile: $\beta_g=1.0_2$ (fixed, $S=1.7$), $\beta_l=3.2$.

Results and Discussion

The spectra of sulfuric acid at all the concentrations studied could be well approximated by a superposition of four Voigt functions with peaks at about 900, 980, 1030, and 1050 cm^{-1}. The observed spectral intensities of sulfuric acid at several concentrations are shown in Fig. 2. Examples of the band resolution are shown in Figs. 3 and 4. Chen and Irish[3,4] reported that each component could be best approximated by a Lorentz-Gaussian product function whose wing falls much faster than that of the Voigt function. The bands observed in those studies might be deformed as a result of the larger slit widths.

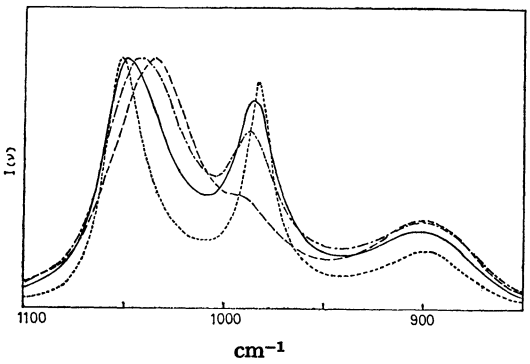

Fig. 2. Observed Raman bands of sulfuric acid. The intensities of the peaks at about 1050 cm^{-1} are normalized.
---- 1.4 M, —— 5.2 M, —·— 7.3 M, ——— 10.6 M.

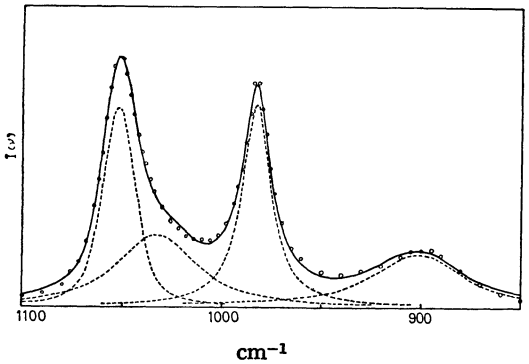

Fig. 3. Resolution of the band for 1.4 M sulfuric acid.
o o o Observed intensity, ---- calculated component intensity, —— calculated total intensity.

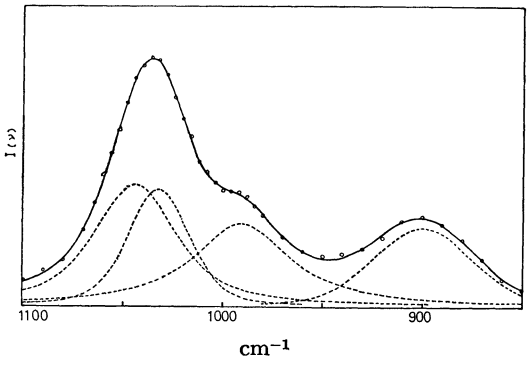

Fig. 4. Resolution of the band for 10.6 M sulfuric acid.
o o o Observed intensity, ---- calculated component intensity, —— calculated total intensity.

The band at about 980 cm^{-1} is assigned to the symmetric stretching vibration of SO_4^{2-}, while the bands at about 1050 cm^{-1} and 900 cm^{-1} are assigned to HSO_4^-.[9-11] The fourth band, at about 1030 cm^{-1}, was first found by Irish and Chen[3,4] and was assigned to the $H_3O^+ \cdot HSO_4^-$ ion pair. They identified an additional weak band near 950 cm^{-1}. However, its counterpart was not recognized in the present analysis.[12]

With an increase in the concentration of sulfuric acid from 0.5 to 10.6 M, the SO_4^{2-} band shifts from 982 to 991 cm^{-1}. On the other hand, the frequency of the HSO_4^- band near 1050 cm^{-1} is lowered from 1052 to 1044 cm^{-1}. These facts suggest that the S–O bond strength in SO_4^{2-} and HSO_4^- is affected by their ionic atmosphere in an opposite manner.

The concentration-half-width curves for the 980 and 1050 cm^{-1} bands are shown in Figs. 5 and 6 respectively. In the simulation of the bands, the uncertainty involved in the background line and the strong correlation between the bands at 1050 and 1030 cm^{-1} more or less obscure the best values of the half-widths. How-

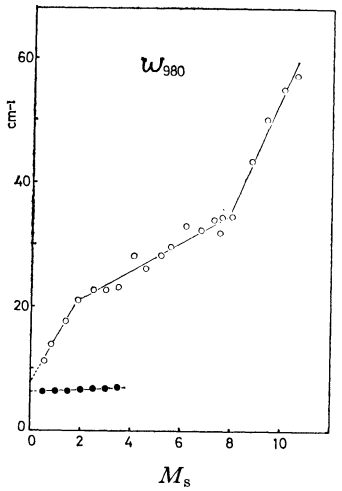

Fig. 5. Concentration dependence of the half-width of the 980 cm^{-1} band.
○: Sulfuric acid, ●: ammonium sulfate.

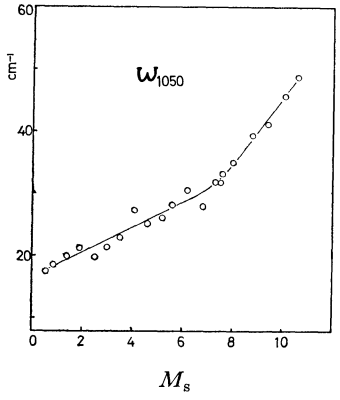

Fig. 6. Concentration dependence of the half-width o the 1050 cm^{-1} band of sulfuric acid.

ever, their influences are insignificant on the results obtained for the narrower bands appearing as plain peaks in the observed spectra. As for the 1050 cm^{-1} band, its half-width values in the range beyond 7 M probably have large errors.

The concentration-half-width curve for the 980 cm^{-1} band of H_2SO_4 in solutions has two conspicuous bends, at about 2 M and 8 M, in the stoichiometric concentration. The bend at the lower concentration has already been reported by Chen and Irish,[4] but the bend at 8 M has not been reported previously. The extrapolation of the curve to a zero concentration gives $\omega_0 = 8.0 \pm 0.3$ cm^{-1}. This value is close to that for the aqueous solutions of $(NH_4)_2SO_4$, 6.3 cm^{-1}. As for the 980 cm^{-1} band of the salt solutions, its half-width shows only a slight change, from 6.3 to 7.0 cm^{-1}, as the concentration increases from 0.5 to 3.5 M, and its band center is located almost consistently at 980.5 cm^{-1}. These half-widths are about half for $(NH_4)_2SO_4$ solutions and about 30% smaller for H_2SO_4 solutions as compared with the half-widths reported in the previous papers.[3,4]

Since the symmetry of SO_4^{2-} in aqueous solutions is regular tetrahedral,[13] the width of the totally symmetric stretching band at 980 cm^{-1} must not be affected by the reorientational motion of the ion.[14,15] Therefore, the broadening of the 980 cm^{-1} band is probably caused by the chemical process that extinguishes the SO_4^{2-} ion in the following equilibrium:

$$H_3O^+ + SO_4^{2-} \rightleftharpoons HSO_4^- + H_2O,$$

and by other mechanisms such as the vibrational relaxation.[16] Thus, the ω_0 may be considered to be the linewidth without the broadening due to the chemical process, and the value of $\omega - \omega_0$ for sulfuric acid is related to the mean lifetime, τ, of SO_4^{2-} by the equation:[14]

$$\omega - \omega_0 = 1/\pi c\tau \qquad (2)$$

where c is the velocity of light. The rate constant of proton transfer is given by:[1-4]

$$K_p = \pi c(\omega - \omega_0)/[H_3O^+]. \qquad (3)$$

By making use of values of $[H_3O^+]$ corresponding to the stoichiometric concentration of H_2SO_4, M_s, in the table presented by Chen and Irish[4], the K_p values were calculated; they are plotted against M_s in Fig. 7. The value of $K_p/\pi c$ at M_s values lower than 2 is 5.6 ± 0.2 M^{-1} cm^{-1} ($K_p = 5.3 \times 10^{11}$ M^{-1} s^{-1}), almost independent of the concentration. This value agrees well with that reported by Chen and Irish,[4] 5.8 M^{-1} cm^{-1}, in spite of the large differences in individual ω and ω_0 values between the two studies.[17] The value of K_p begins to decrease abruptly at about $M_s = 2$, corresponding to a bending in the concentration-half-width curve in Fig. 5. According to Eigen and collaborators,[18,19] the rate of proton transfer is much faster in ice than in liquid water because the chains of hydrogen bonds favorable for proton transfer are always arranged in ice. On the other hand, Robertson and Dunford[20] have pointed out, on the basis of their study of the Hammet acidity function of sulfuric acid, that the water clusters disappear rather abruptly at about $M_s = 2$. The results of the present study and the two earlier studies suggest that

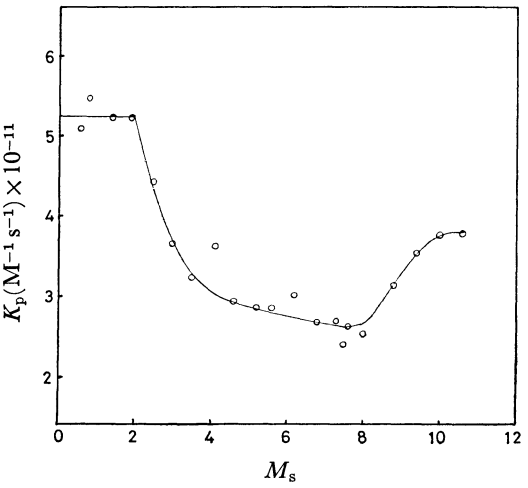

Fig. 7. Concentration dependence of the rate constant $K_p = \pi c(\omega - \omega_0)_{980}/[H_3O^+]$.

the water clusters participate actively in the proton transfer in aqueous solutions of H_2SO_4 because such clusters contain hydrogen-bond networks, even though their sizes are smaller than those in ice. Robertson and Dunford have also found that the average hydration number of the proton in sulfuric acid solutions becomes smaller than four at concentrations beyond $M_s = 8$. This means that a partial defect occurs in the primary hydration shell composed of the four water molecules which stabilize the proton in dilute solutions.[18] Such a defect may activate the proton to react rapidly with SO_4^{2-}. The rise of K_p in concentrated solutions beyond $M_s = 8$ may, then, be attributable to an increase in the defect of the hydration shells about the protons.

If the mean lifetime of HSO_4^- is limited only by the dissociation process,

$$HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$$

then the following two relations hold[4]:

$$[1/\tau(HSO_4^-)] \cdot [HSO_4^-] = [1/\tau(SO_4^{2-})] \cdot [SO_4^{2-}] \qquad (4)$$

for the mean lifetime and:

$$(\omega - \omega_0)_{1050} = A(\omega - \omega_0)_{980} \qquad (5)$$

for the half-width, where

$$A = [SO_4^{2-}]/[HSO_4^-] = ([H_3O^+] - [H_2SO_4])/(2[H_2SO_4] - [H_3O^+]),$$

and where ω_0 is the broadening due to certain causes other than the above reaction. The ω_{1050} values in the $M_s < 7$ range, where they are fairly reliable, are plotted against the values of $A \cdot (\omega - \omega_0)_{980}$ in Fig. 8. If the value of $(\omega_0)_{1050}$ is independent of the concentration, the slope of the curve ought to be unity, as is shown by a broken line in Fig. 8. The observed curve has a slope of about 1.6; it can hardly be considered to have a slope of unity. Therefore, we cannot but consider that the value of $(\omega_0)_{1050}$ increases with the concentration. As has been described previously, the broadening of the SO_4^{2-} band due to any causes other than a chemical process does not vary remarkably with the concentration. Therefore, there seems to be another chemical process which serves

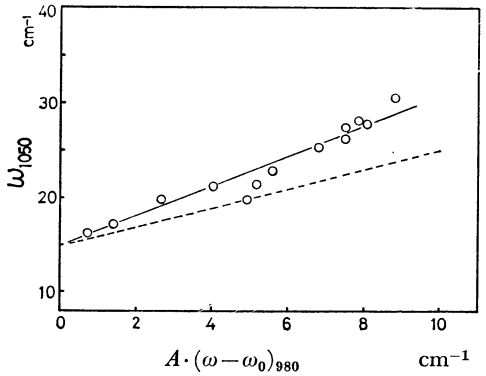

Fig. 8. Interrelation between ω_{1050} and $A\cdot(\omega-\omega_0)_{980}$. The broken line shows a slope of unity.

to shorten the spectroscopic lifetime of HSO_4^-. It seems that the process of forming the $HSO_4^-\cdot H_3O^+$ ion pair is related to the decrease in this spectroscopic lifetime and to the increase in the $(\omega_0)_{1050}$ with concentration.

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12) Since the dissociation process
$$H_3O^+\cdot SO_4^{2-} \rightleftharpoons H_2O + HSO_4^-$$
may proceed much faster than the process
$$H_3O^+\cdot HSO_4^- \rightleftharpoons H_2O + H_2SO_4$$
in aqueous solutions of sulfuric acid below 14 M (see Ref. 11), the $H_3O^+\cdot SO_4^{2-}$ ion pair is considered to be much more unstable than the $H_3O^+\cdot HSO_4^-$ ion pair assigned the 1030 cm^{-1} band at the concentrations employed in the present study. Therefore, a band due to the $H_3O^+\cdot SO_4^{2-}$ ion pair, if it exists, is possibly so weak and broad that it cannot be recognized.
13) See, *e.g.*, G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand and Company, Princeton, N. J. (1945).
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16) The half-width of the 980 cm^{-1} band of the salt solutions should not be broadened by any chemical reaction, but in fact it changes slightly with an increase in the concentration, as was mentioned in the last paragraph. There seem to be several factors influencing the half-width in aqueous solutions in association with the concentration or the structure of aqueous solutions.
17) The observed band is expressed by a convolution of the spectral slit function and the true band-shape function; see Ref. 8. The observed half-width is, in general, smaller than the sum of the half-widths of the two functions. The ω and ω_0, and accordingly $\omega-\omega_0$, are influenced by the finite spectral slit width.
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