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National Defense Academy of Japan

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Complete ionization of concentrated sulfuric acid at low temperatures

H. Kanno

Department of Chemistry, National Defense Academy, Yokosuka, Kanagawa 239, Japan

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Raman measurements were carried out on glassy concentrated sulfuric acid ($R=3, 6$ and 10 , R =moles of water/moles of H_2SO_4). It is shown that complete ionization of concentrated sulfuric acid is realized at low temperatures.

1. Introduction

It is well known that strong inorganic acids such as nitric, sulfuric and hydrochloric acids dissociate completely in water at dilute acid concentrations [1]. However, in the case of sulfuric acid of medium acid concentration, an appreciable amount of HSO_4^- ions exists at ordinary temperatures as we expect from $\log K_2 = -1.99$ (at $25^\circ C$) [2]. In a recent Raman study by Irish and coworkers [3], it is reported that the population of HSO_4^- ions increases at elevated temperatures and pressures. They also studied nitric acid up to high temperatures and pressures and reported that the intensities of Raman bands of molecular HNO_3 increase with rise in temperature [4]. On the other hand, ionization of weak acids such as boric, carbonic and acetic acids increases with rise in temperature [2]. In view of these observations [3,4], we are tempted to consider how the ionization of a concentrated strong acid will change at low temperatures. The present study reveals that complete ionization of concentrated sulfuric acid is realized at low temperatures (below $-100^\circ C$), that is, even HSO_4^- ions convert into oxonium ions and SO_4^{2-} ions at low temperatures.

Raman spectroscopy is here employed to investigate the ionization of concentrated sulfuric acid at low temperatures.

2. Experimental

Aqueous H_2SO_4 solutions of the concentrations $R=3, 6$ and 10 (R =moles of water/moles of H_2SO_4) were prepared from 98 wt% H_2SO_4 of guaranteed grade by diluting with distilled water. Raman measurements were carried out with a NR-1100 Raman spectrometer using ≈ 300 mW of the 514.5 nm line of a NEC argon ion laser as an exciting source.

In obtaining Raman spectra of glassy samples, we used a special quartz Dewar vessel designed specifically to maintain the glassy sample solution at liquid nitrogen temperature during the Raman measurements. Vitrification of a sample solution was achieved by immersing an aliquot of the sample solution in a 4–5 mm inner diameter Raman cell in liquid nitrogen. The overall cooling rate of the sample was about 4×10^2 K/min. The details of the Raman measurements of the glassy samples were essentially the same as previously reported [5].

3. Results and discussion

To visualize the Raman results obtained in this work, the Raman spectra of concentrated sulfuric acids ($R=3, 6$ and 10) at room temperature are shown in fig. 1. The Raman band at 1052 cm^{-1} , which is assigned to the symmetric SO_3 stretching mode of HSO_4^- ions, is the strongest among all Raman bands and increases in intensity relative to the

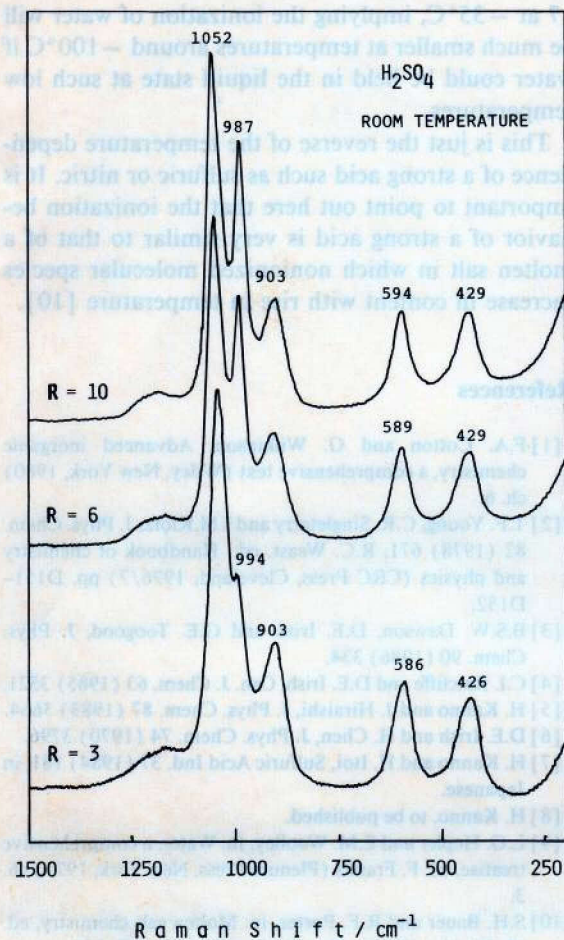


Fig. 1. Raman spectra of concentrated sulfuric acids ($R=3, 6$, and 10) at room temperature.

Raman band at 987 cm^{-1} , which is the ν_1 band (the symmetric stretching vibration) of SO_4^{2-} ions, with decreasing R (increasing in H_2SO_4 concentration).

This is consistent with a previous report: Irish and Chen [6] observed that the ν_1 band (at 1052 cm^{-1}) of HSO_4^- ions is already higher than that (at 987 cm^{-1}) of SO_4^{2-} ions in $2\text{ M H}_2\text{SO}_4$ solution at room temperature. In other words, the second stage dissociation of sulfuric acid is incomplete even in relatively low acid concentration ranges.

Raman spectra of glassy aqueous H_2SO_4 solutions ($R=3$ and 6) are shown in fig. 2. It can be noted that the quality of the Raman spectrum for the $R=3$ solution is not good because of the interfering flu-

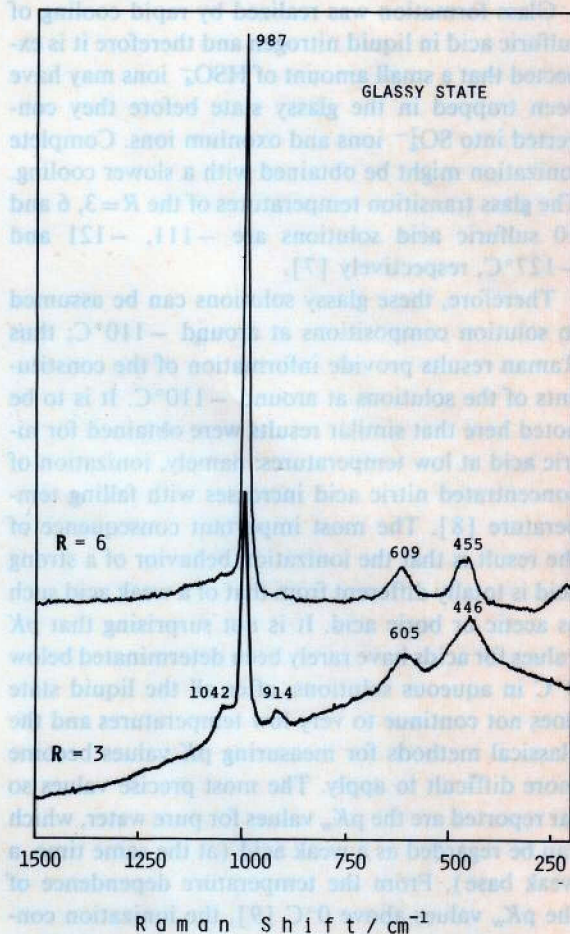


Fig. 2. Raman spectra of glassy sulfuric acids ($R=3$ and 6) at liquid nitrogen temperature.

orescence spectrum which is unavoidable for glassy concentrated sulfuric acid solutions.

We immediately know that the Raman bands ascribable to HSO_4^- ions almost disappeared on vitrification, indicating that sulfuric acid dissociates almost completely into oxonium and sulfate ions (H_3O^+ and SO_4^{2-} ions) in glassy sulfuric acid.

Sharpness of the Raman band at 987 cm^{-1} is also a strong support for the contention that ionization of concentrated H_2SO_4 is almost complete at low temperatures. In the Raman spectrum for the glassy sulfuric acid with $R=3$, weak Raman bands are observed at 914 and 1042 cm^{-1} and are evidently due to traces of HSO_4^- ions.

Glass formation was realized by rapid cooling of sulfuric acid in liquid nitrogen and therefore it is expected that a small amount of HSO_4^- ions may have been trapped in the glassy state before they converted into SO_4^{2-} ions and oxonium ions. Complete ionization might be obtained with a slower cooling. The glass transition temperatures of the $R=3$, 6 and 10 sulfuric acid solutions are -111 , -121 and -127°C , respectively [7].

Therefore, these glassy solutions can be assumed to solution compositions at around -110°C ; thus Raman results provide information of the constituents of the solutions at around -110°C . It is to be noted here that similar results were obtained for nitric acid at low temperatures: namely, ionization of concentrated nitric acid increases with falling temperature [8]. The most important consequence of the result is that the ionization behavior of a strong acid is totally different from that of a weak acid such as acetic or boric acid. It is not surprising that pK values for acids have rarely been determined below 0°C in aqueous solutions; after all the liquid state does not continue to very low temperatures and the classical methods for measuring pK values become more difficult to apply. The most precise values so far reported are the pK_w values for pure water, which can be regarded as a weak acid (at the same time, a weak base). From the temperature dependence of the pK_w values above 0°C [9], the ionization constant (pK_w) for water increases from 14 at 25°C to

17 at -35°C , implying the ionization of water will be much smaller at temperatures around -100°C if water could be held in the liquid state at such low temperatures.

This is just the reverse of the temperature dependence of a strong acid such as sulfuric or nitric. It is important to point out here that the ionization behavior of a strong acid is very similar to that of a molten salt in which nonionized molecular species increase in content with rise in temperature [10].

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