

A Raman Experiment exploring the Definition of a Strong Acid

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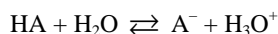
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Abstract: Raman spectra of the “strong” acids HNO₃, HClO₄, and H₂SO₄ are collected and analyzed for high concentration solutions. The spectra display the presence of peaks corresponding to undissociated acid species in solution. Quantitatively, we can determine the equilibrium constant for these acids to be less than the infinite value expected for a completely dissociated species. We call for a revision to the conditions for a “strong” acid as being completely dissociated, to one having significant dissociation at a specific concentration (for example, 1 molar).

Typical general chemistry texts define a strong acid as being a strong electrolyte, that being defined as a species which is completely dissociated, typically in aqueous solution [1, 2]. In terms of the equilibrium considered later, the reaction $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ has a large equilibrium constant, perhaps even immeasurable equilibrium constant. Yet what happens when the molecule ratio of the acid to water comes close to 1:1 in acidic atmospheric cloud formation [3] near the freezing point as occurs in polar stratospheric clouds becomes important chemistry.

Our curiosity was piqued by a sidebar in a textbook [4] noting this effect, and noting that Raman spectroscopy would be a useful tool for examining this phenomenon because of the selection rules governing Raman spectra, namely that for totally symmetric species the Raman spectrum is allowed while the infrared transitions are forbidden. Previous work has examined the Raman spectra of weak acids to examine the acid/base equilibrium for those species [5] and to determine the spectra of the species [6–9]. We choose to look at high concentrations of three of the typical strong acids to examine this phenomenon using a simple Raman spectrometer (Delta Nu) in a laboratory appropriate for the undergraduate physical or analytical chemistry course. We choose to examine HNO₃, HClO₄, and H₂SO₄ spectra at a variety of concentrations because the anion of each (NO₃⁻, ClO₄⁻, and HSO₄⁻) has a readily obtainable Raman spectrum as does the acid itself. Essentially, the equilibrium constant for the dissociation reaction



will be examined by studying the ratio of HA to A⁻ using the Raman spectrum at a variety of total HA concentrations.

Experimentally, this laboratory is quite simple, yet effective. We begin with concentrated acids and dilute them while recording the Raman spectrum as a function of concentration. Using nitric acid as an example; we start with standard concentrated nitric acid. This solution is commonly labeled as 69.8 % or 15.6 M. The corresponding figures for perchloric and sulfuric acids are 70.0 % (12.3 M) and 96.1 % (17.94 M), respectively. Higher and lower concentrations of each of these acids are also available. From the highest concentration of acid

available, a series of dilutions of 1, 2, 3, ..., 10 mL of acid to 10 mL of solution are made. An appropriate amount of the resulting dilute acid solution is placed in a clean, dry Raman sample vial and the Raman spectrum of the solution is collected over the frequency range from 200 to 3400 cm⁻¹. All three acids exhibit Raman signals in this range [6–9] with the HNO₃ and NO₃⁻ signals occurring near (937 and 1280) and 1030 cm⁻¹ respectively, the ClO₄⁻ signals occurring near 930 cm⁻¹, and the HSO₄⁻ signals near 1034 cm⁻¹. It is not necessary to quantitatively prepare the diluted solutions because the second step is to titrate the resulting dilute solutions against a NaOH solution of known concentration to determine the exact molarity of each diluted solution. We conduct the titrations because we have found that simple calculation of the concentration using the dilution formula yields values which are not consistent with the experimentally determined concentrations.

Figures 1–3 display Raman spectra of nitric, perchloric, and sulfuric acid at the indicated concentrations. For a given acid, the peaks corresponding to the associated acid become more prevalent than those of the dissociated acid, the bare anion, as higher concentrations of acid are reached. The relative areas of the peaks corresponding to the dissociated acid and the anion are carefully determined using the software for spectrum manipulation for the Raman instrument by baseline subtraction. It may be necessary to fit peaks to multiple mixed Gaussian/Lorentzian peaks in the event of overlapping peaks. Because the area of the Raman peak is proportional to the concentration, we now have measures of the relative concentration of the associated acid or the anion as a function of the stated concentration of the solution from titration. We do have a relative measure of the two concentrations but not an absolute measure of the ratio because the Raman scattering coefficients for the two species may not be identical.

There are two methods to achieve a calibration curve for species concentration. The first involves mixing a series of highly concentrated solutions containing the anion to create an externally generated calibration curve for the anion concentration. For example, a series of highly concentrated NaNO₃ solutions (up to the maximum solubility of 921 g per 1000 g H₂O or about 6 M) can be generated to study the nitrate anion. Alternatively, we can recognize that the Raman signal is

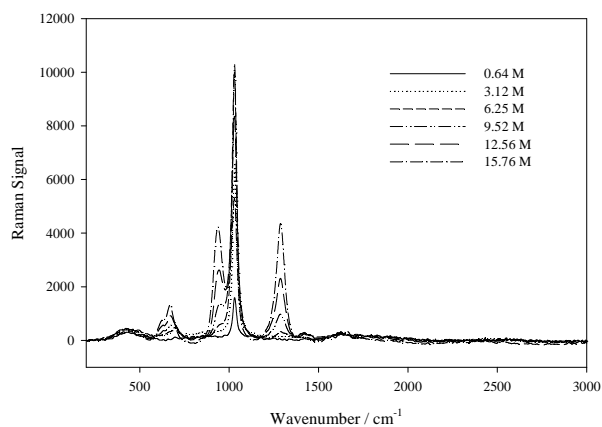


Figure 1. Nitric acid spectra at 0.64, 3.12, 6.25, 9.52, 12.56, and 15.76 molar concentrations.

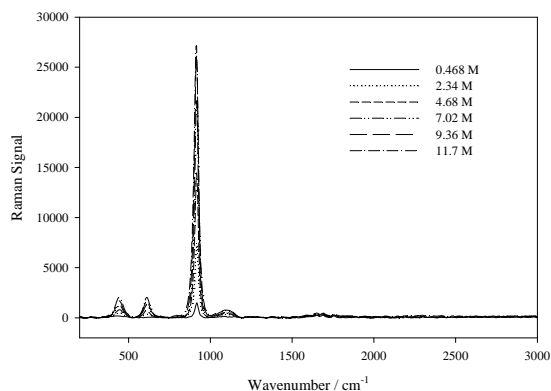


Figure 2. Perchloric acid spectra at 0.468, 2.34, 4.68, 7.02, 9.36, and 11.7 molar concentrations.

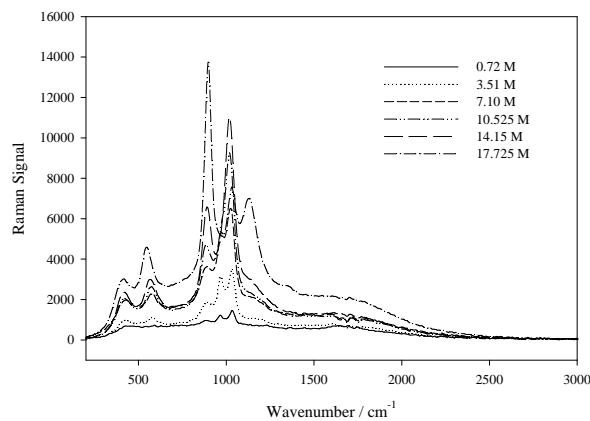


Figure 3. Sulfuric acid spectra at 0.72, 3.51, 7.10, 10.525, 14.15, and 17.725 molar concentrations.

linear with concentration, and that the total acid concentration / anion concentration is known to generate an internal calibration curve. Figure 4 shows experimental data on Raman peak area against solution concentration obtained from the already performed titrations. The nitric acid data are shown in Figure 4 because they display the deviation from linearity of

the Raman signals most clearly. Superimposed on the experimental data is the straight line obtained by extrapolating the data from the lowest concentrations. Most importantly for us, the absolute ratio of the associated acid and anion concentrations can be obtained from the distance between the extrapolation and experimental peak area to the distance between the experimental peak area and zero for peaks of the anion as shown. This would be reversed if the spectroscopic peak is one associated with the associated acid species. The plot for H_2SO_4 is complicated by observation of a peak corresponding to HSO_4^- and the multiple equilibria involved.

We now have information on the absolute concentration of associated acid and anion from an internal or external calibration. Figure 5 displays data on the ratio of the associated acid to anion concentration as a function of solution concentration for nitric acid. If the strong acid involved is completely dissociated at all concentrations, such a plot would be zero and unchanging with solution concentration. The departure from this prediction indicates that the acid must be partially associated at higher concentrations. A similar plot is obtained for HClO_4 . The departure is also qualitatively observed in the Raman spectra as peaks corresponding to the associated acid grow in at higher concentration relative to the anion peaks. The K_a values obtained from an average of the points at highest concentration are thus 11(24 for HNO_3), and 150 (complete dissociation to 10 M, 64000 for $\text{HClO}_4 \cdot 3\text{H}_2\text{O}$, 132 for $\text{HClO}_4 \cdot 7\text{H}_2\text{O}$) for HNO_3 and HClO_4 respectively. The H_2SO_4 data do not lend themselves to a similar analysis for the reasons mentioned above. The literature values are in parenthesis [10]. Note that the values are not infinite as would occur if the acid were completely dissociated. Qualitatively, this same effect is observed in the presence of Raman peaks associated with the undissociated acid.

Now that we have determined that the acids are not completely dissociated, despite their classification as strong acids, we ask why this phenomenon would occur. We begin by calculating the ratio of the number of water molecules to the number of acid molecules in the most concentrated solutions. Using the molarities, and densities of the concentrated solutions given earlier, we obtain ratios of 1.56:1, 0.42:1, and 4.53:1 for $\text{HNO}_3:\text{H}_2\text{O}$, $\text{HClO}_4:\text{H}_2\text{O}$, and $\text{H}_2\text{SO}_4:\text{H}_2\text{O}$ respectively. These ratios suggest that there are approximately the same number of water molecules in the solution as acid molecules. Thus there are insufficient water molecules to interact with all the protons released on acid dissociation. Thus it would be surprising if this lack of dissociation was not observed at high concentrations, and that a “strong” acid needs to be more carefully defined.

In summary, we have demonstrated that Raman spectroscopy is a useful tool for the detection and quantitation of signals from the symmetric species involved in these dissociations and that some interesting chemistry is demonstrated. Lastly, we and others have shown that the adjective “strong”, defined by completely dissociated, is a misconception in this case.

Safety

The high concentration solutions of acid used in this laboratory require extreme caution in their handling because of their reactivity. Appropriate safety precautions must be taken in handling all the solutions in the laboratory.

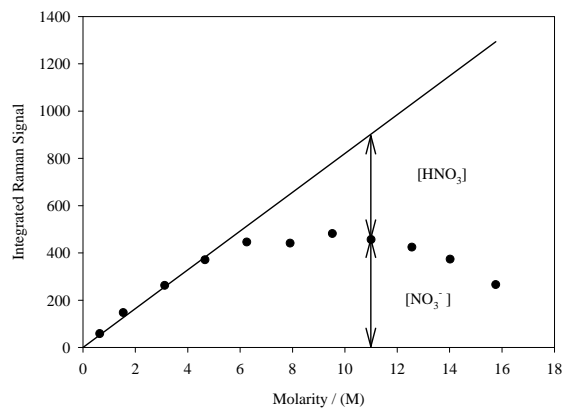


Figure 4. Plot of the Raman signal against molarity showing the relative concentration of HNO_3 and NO_3^- at a given concentration.

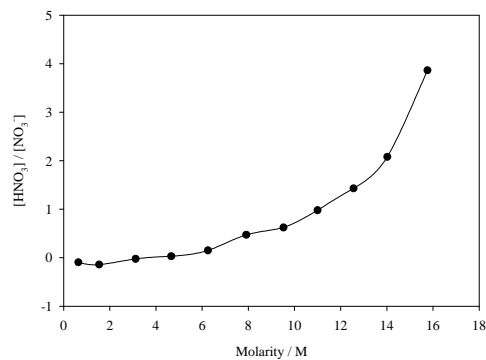


Figure 5. $[\text{HNO}_3] : [\text{NO}_3^-]$ as a function of HNO_3 concentration.

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References and Notes

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