Deuterium Isotope Effects on Acid Ionization and Transition Metal Hydrolysis at Reactor Conditions by Raman Spectroscopy

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Abstract

This paper reports the preliminary measurements from an experimental study to measure the small differences between light (H_2O) and heavy (D_2O) water under reactor operating conditions (250-300 ^oC, 10 MPa), using Raman spectroscopy. The deuterium isotope effect $\Delta pK = pK_{D_2O} - pK_{H_2O}$, for sodium bisulphate $NaDSO_4$ and phosphoric acid D_3PO_4, has now been determined at temperatures of 25 ^oC and 80 ^oC by measuring the isotropic Raman spectra at different concentrations. The results for the pK and ΔpK at 25 ^oC agree with the literature, confirming the reliability of the method. High temperature cells have been constructed.

1. Introduction

Increasing pressure on critical fuel reserves has initiated efforts to produce efficient and environmentally friendly methods of energy production. This area of research plays a vital role for future generations as concerns with energy demands and population growth continue to be a primary global issue. Sustainable energy completely derived from natural resources would alleviate our dependency on fossil fuels but the technology for this to happen is still not available [1]. Therefore, considerable attention must be made to maximize the efficiency of existing energy production methods. The CANDU line of reactors will play a pivotal role towards the shift from fossil fuels to environmentally sustainable resources. These reactors produce essentially zero carbon emissions and are designed to continue operating during refueling [1].

A thorough knowledge of the water chemistry at the elevated temperatures of reactor operation is needed to reduce the effects of flow accelerated corrosion (FAC) inside the feeder tubes [2]. The mechanisms of FAC has not yet been fully investigated, however, major contributors to the problem have been identified such as water chemistry, hydrodynamics, materials and temperature [3]. The purpose of this research is to increase the longevity of the CANDU reactors by providing an experimental model for metal hydrolysis that occurs inside the feeder tubes. The solubility of the thin layer of magnetite inside the feeder tube has been shown to have a delicate dependency on the water pH [4]. The solubility of magnetite is so small that differences between D_2O and H_2O cannot be measured with sufficient accuracy to determine the pH needed to minimize feeder tube thinning while avoiding in core deposition. At present, the optimum value is estimated from light water loop experiments.

The ΔpK values are defined by the following equation:

$$\Delta pK = pK_{D_2O} - pK_{H_2O} \tag{1}$$

Current ΔpK values used by the nuclear industry apply an “apparent” value that has been tabulated by Laughton and Robertson at 25 ^{o}C and gives an average value of 0.46 as shown in Figure 1. Literature values for ΔpK have only been measured for a handful of species above 25 ^{o}C and these are plotted in Figure2 [5-7].

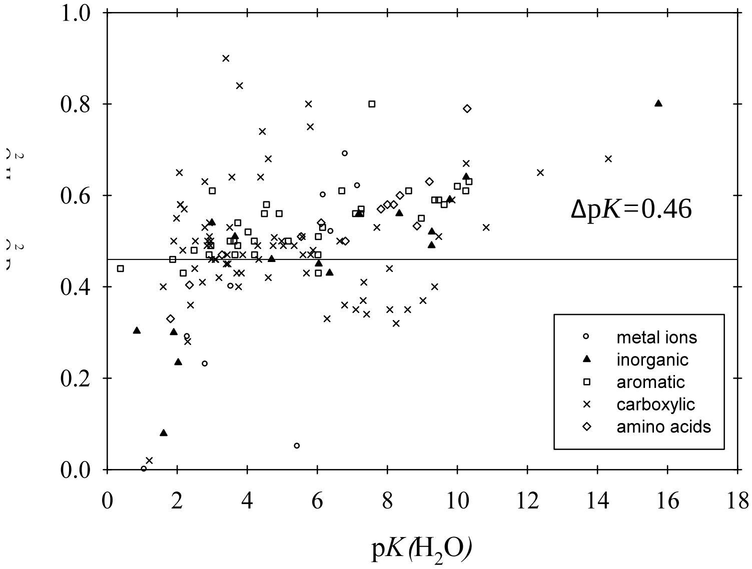

Figure 1 ΔpK values calculated at 25 ^{o}C for various weak electrolytes

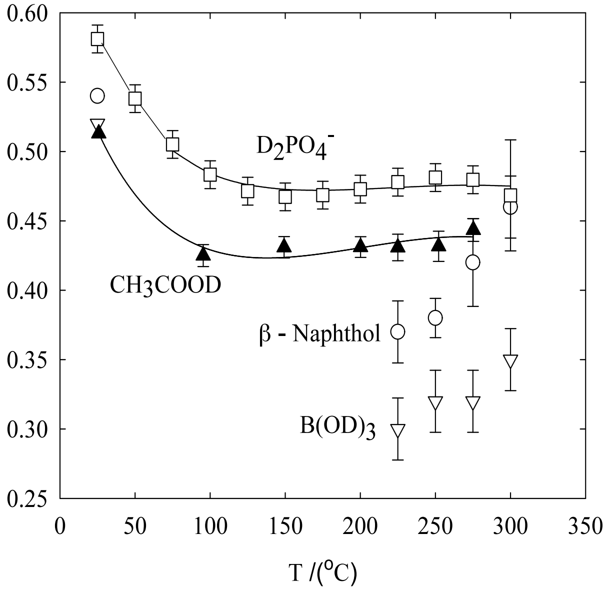

Figure 2 Previous ΔpK values as a function of temperature [Erickson et al., [5] (▲) ; Mesmer and Herting, [6] (□) and Bulemela and Tremaine, [7] (○,∨)]

ΔpK values reported in Figure 2 are based on conductance measurements and colorimetric indicators using UV/Vis spectroscopy. The conductance measurements provide extremely accurate results and can detect concentrations on the order of 10^{-7} mol kg^{-1}. However, this technique provides no structural information and, due to the sensitivity of the apparatus, is inherently responsive to impurities. Bulemela *et al.*, [7] measured boric acid and beta-naphthol systems by UV-visible methods. UV-visible experiments require colorimetric indicators that are stable at high temperatures and pressures, however, the buffers needed for heavy water calibration are extremely limited.

In addition with the two previously mentioned techniques Raman spectroscopy will also be employed as a complimentary tool. Structural information such as symmetry and bonding characteristics are all valuable characteristics that can be probed by Raman method [8]. The measurements can also be conducted using concentrated acids/bases or supporting electrolyte solutions and issues involving impurities are minimal. An inherent challenge that comes with Raman spectroscopy is the limits of detection. The lowest concentration that will produce a reliable spectra is on the order of 0.01 mol kg^{-1}. At this concentration the ionic strength of the solution must be accounted for and methods of dealing with activity coefficients will have to be applied.

The purpose of this research is to provide ΔpK results from various weak electrolytes that are chemically similar to the reaction of magnetite hydrolysis. These experiments will be conducted at ambient temperatures and increase to the operating ranges of the CANDU reactors.

2. Experimental

2.1 Solution preparation

The sodium hydrogensulfate monohydrate (99%) samples were purchased from Sigma-Aldrich and dried to constant mass in an oven. Light water (H_2O) sample were prepared using a Millipore water purifying system. The heavy water is supplied by AECL and the samples are prepared in a glove bag under an inert atmosphere (argon) to prevent atmospheric H_2O contamination. Heavy water samples are then determined for purity using NMR. The H_3PO_4/ D_3PO_4 and Na_3PO_4 solutions were prepared in the same manner as bisulfate.

Aquamolality has been chosen as the standard state and is defined as the moles of solute/55.51 moles of solvent. The use of aquamolality[‡], m_{aq}, instead of molality, m, allows thermodynamic properties in the two solvents to be compared at the same mole fraction of solute molecules.

[‡] $m_{aq} = m$ in H_2O and $m_{aq} = 1.1117\ m$ in D_2O

2.2 Raman spectroscopy

Experiments were performed using the HR-LabRam instrument, (Model T64000) from Horiba Jobin Yvon Ltd. Irradiation of the sample was conducted using a 250 mW argon laser that produces a wavelength of 532 nm.

Samples of the weak acids for light and heavy water were loaded into glass tubes under an argon atmosphere in a glove bag. The samples are sealed inside a glass tube and then are placed within the macrochamber (shown in figure 3b) to be measured. The temperature of the sample is controlled by a Peltier. A collecting lens is located 90^{o} to the incident radiation where the Raman scattered radiation is focused to a CCD detector. The proposed split cell design shown in figure 3a will eliminate systematic errors while measuring the ΔpK values between light and heavy water. Any temperature fluctuations will happen in unison between the two cells and the errors will cancel out.

A transition will be visible in the Raman spectrum only if there is a change in polarizability along the axis of vibration [8]. This selection rule can be quantified. The spectra are collected with the polarizer in two different configurations, parallel and perpendicular to the incident light to acquire the isotropic spectra [9] as seen in Figure 4. By combining these two spectra, the asymmetric bands and most of the unwanted background can be removed. The resulting “isotropic” spectra shows only the symmetric vibration of each species.

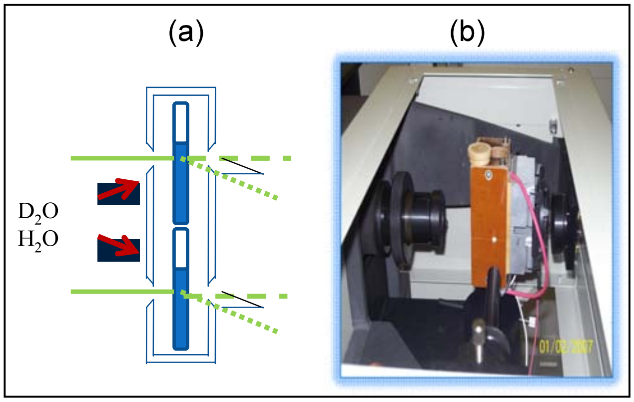

Figure 3 The proposed split cell design will analyze both light and heavy water simultaneously

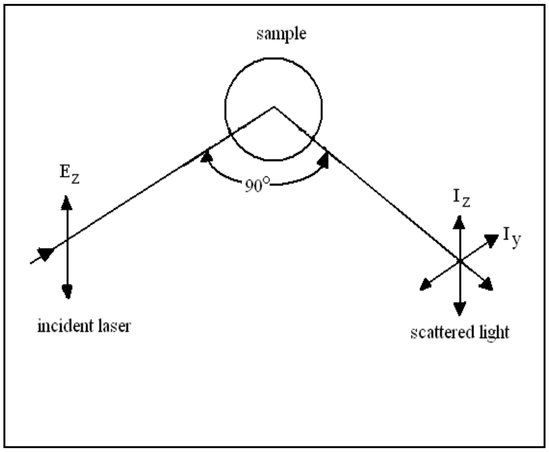

Figure 4 The parallel (I_z) and perpendicular (I_y) scattered radiation

3. Results and Discussion

3.1 Isotropic spectra and deconvolution

The “isotropic” spectra is calculated from the parallel and perpendicular scattered intensities (Figure 5) according to the following relationship [10]:

$$I(\bar{\nu})(iso) = R(\bar{\nu})_{\|} - (4/3)R(\bar{\nu})_{\perp} \tag{3}$$

Where $R(\bar{\nu})_{\|}$ and $R(\bar{\nu})_{\perp}$ are the parallel and perpendicular reduced spectra, respectively:

$$R(\bar{\nu})_{\|} = I_{\|}(\bar{\nu})(\bar{\nu}_o - \bar{\nu}_i)^{-4}(\bar{\nu})^4 B \tag{4}$$

$$R(\bar{\nu})_{\perp} = I_{\perp}(\bar{\nu})(\bar{\nu}_o - \bar{\nu}_i)^{-4}(\bar{\nu})^4 B \tag{5}$$

where $\bar{\nu}_o$ and $\bar{\nu}$ are the absolute frequency (in cm^{-1}) of the excitation laser and scattered light, respectively. This correction accounts for the temperature dependence of excited vibrational states and Rayleigh scattering. The B term is defined below and contains the Boltzman distribution term:

$$B = 1 - \exp\left(-\frac{h\bar{\nu}_i c}{kT}\right) \tag{6}$$

The deconvolution of spectra was performed by the computer software Origin. The function used for the bisulphate study was chosen to be PSVOIGHT. The primary motives of this chose were to combine Gaussian and Lorentzian functions. Figure 6 shows the spectral deconvolution of the isotropic spectrum for 0.1 mol kg^{-1} bisulfate solution at 25 ^oC.

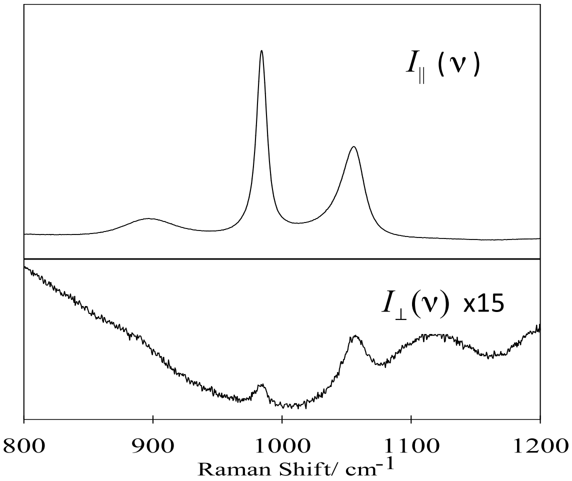

Figure 5 the parallel (x1) and perpendicular (x15) spectra for the bisulfate solution at 25 ^oC

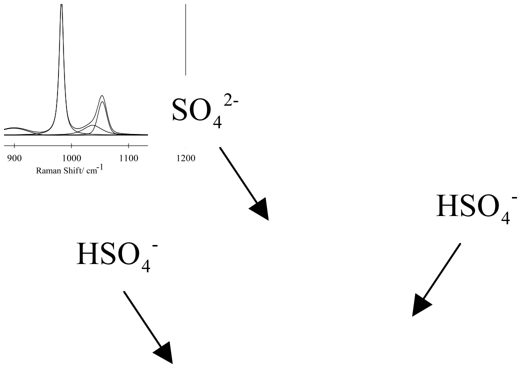

Figure 6 Raman spectra for 0.1 mol kg^{-1} bisulfate solution showing the symmetric vibrations due to SO_4^{2-} and HSO_4^- and the deconvolution using Origin at 25 ^oC.

3.2 Isotopic effects in bisulfate equilibrium

Isotropic spectra were measured for bisulfate solutions in light and heavy water. The most intense symmetric peaks at 980 cm^{-1} and 1050 cm^{-1} were used for quantitative measurements as shown in Figure 7. Although hydrogen and deuterium closely resemble each other they have very distinct chemical and physical characteristics as can be seen from the difference in Raman shifts between the two solutions. The mass of deuterium is approximately doubled due to the additional neutron. This addition changes the reduced mass and, ultimately, the vibrational energy compared to hydrogen resulting in unique chemical properties.

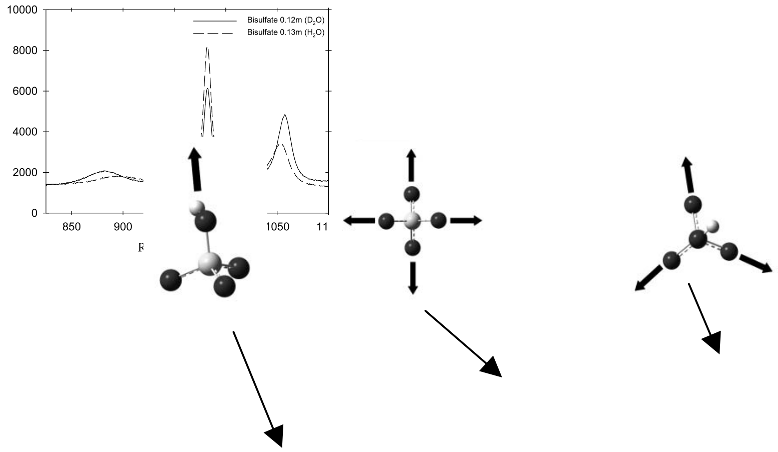

Figure 7 Vibrational modes with coresponding peaks for bisulphate in light (0.13 m) and heavy (0.12 mol kg^{-1}) water at 25 °C

3.3 Determination of the equilibrium constant

The bisulfate equilibrium is represented by the following expression:

$$HSO_4^{-}(aq) \rightleftharpoons H^{+}(aq) + SO_4^{2-}(aq) \qquad (7)$$

$$1-\alpha \qquad\qquad \alpha \qquad\qquad \alpha$$

The degree of dissociation, α, is the fraction of deprotonated bisulphate at equilibrium.

The equilibrium constant, K_2, is defined as:

$$K_2 = \frac{a_{H^+} a_{SO_4^{2-}}}{a_{HSO_4^-}} = Q_m Q_\gamma = \frac{m_{H^+} m_{SO_4^{2-}}}{m_{HSO_4^-}} \frac{\gamma_{H^+} \gamma_{SO_4^{2-}}}{\gamma_{HSO_4^-}} \tag{8}$$

where a is the activity of the solute; m is the molality (mol kg^{-1}); γ is the activity coefficient of the solute; Q_m is the equilibrium constant; Q_γ gamma is the activity quotient. The degree of dissociation, initial molality and activity quotient can then be used to derive an equation for the equilibrium constant:

$$K_2 = \frac{\alpha^2 m_{\mathrm{NaHSO_4}}}{1-\alpha} Q_\gamma \tag{9}$$

At equilibrium, the fraction of bisulfate that has dissociated, α, can be acquired from the integrated intensities as seen in equation 10. Previous determinations of the bisulphate equilibrium constant have been studied using the same approach [11] using Raman spectroscopy.

$$I_{HSO4^-} = J_{HSO4^-} m_{HSO4^-} \tag{10}$$

J is the scattering coefficient and dependent on the species and instrumental system used [11]. The scattering coefficient relates the species concentration to the integration of the symmetric peak intensities, I. Taking the ratio of the species under analysis produces the RJ term located in equation 13 where it can then be applied to determine α (equation 12).

$$m_{SO4^{2-}} / m_{HSO4^-} = \left(I_{SO4^{2-}} / I_{HSO4^-}\right)\left(J_{HSO4^-} / J_{SO4^{2-}}\right) = RJ \tag{11}$$

$$\alpha = RJ / \left(1 + RJ\right) \tag{12}$$

Figure 8 shows the Δp*K* results for the bisulfate system as a function of temperature assuming that the ratio of activity coefficients between light and heavy water are equal to one for a wide range of aquamolal concentrations. For dilute solutions Δp*K* values were found to be relatively constant Δp*K* = 0.37 ± 0.02 up to 80 $^{\circ}$C, Figure 9. This is in agreement with the value of 0.3 [12]

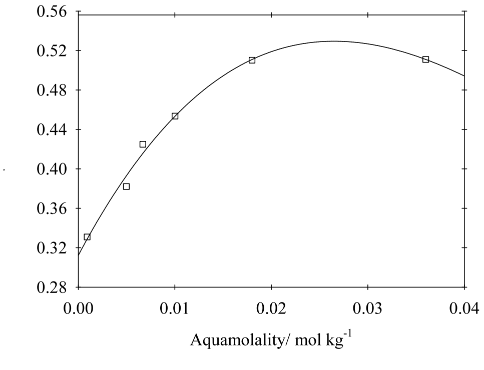

Figure 8 Δp*K* values as a function of aquamolality for bisulphate at 25°C

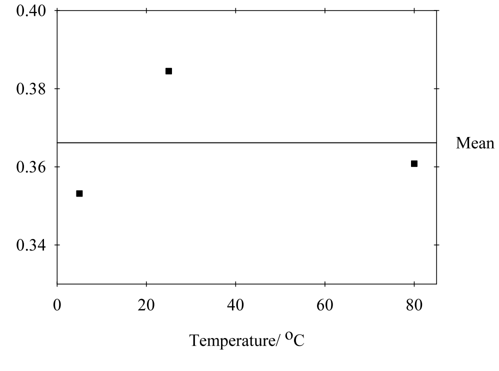

Figure 9 Δp*K* as a function of temperature for bisulfate (0.13 m)

3.4 Temperature Effects on Equilibrium Constant

Bisulfate dissociation constants can be expressed in the isocoulombic form using dissociation constants for light and heavy water, log Q_w [13] and log Q_D [6] as shown in equations 13 and 14. By keeping the charges of the equation symmetrical the effects of the ionic strength for the solution is minimized:

$$K_{isoHSO_4} = \frac{K_{2HSO_4}}{K_w} = \frac{Q_{2HSO_4}}{Q_w} \qquad (13)$$

$$K_{isoDSO_4} = \frac{K_{2DSO_4}}{K_D} = \frac{Q_{2DSO_4}}{Q_D} \qquad (14)$$

The isocoulombic equilibrium constant has a temperature dependence that is described by the van't Hoff equation:

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^o}{RT^2} \qquad (15)$$

Where ΔH^o is the standard enthalpy; R is the gas constant and T is temperature. Figure 10 and 11 shows the temperature effects on the bisulphate system. As the temperature is increased from 25 °C to 80 °C the dominant component in solution becomes the protonated bisulphate species.

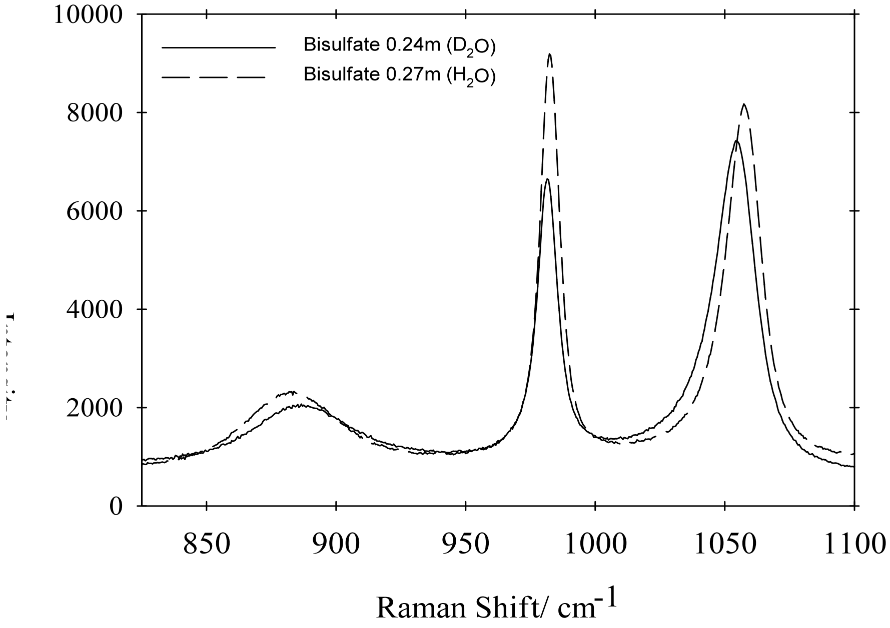

Figure 10 Bisulfate in light and heavy water at 25 °C

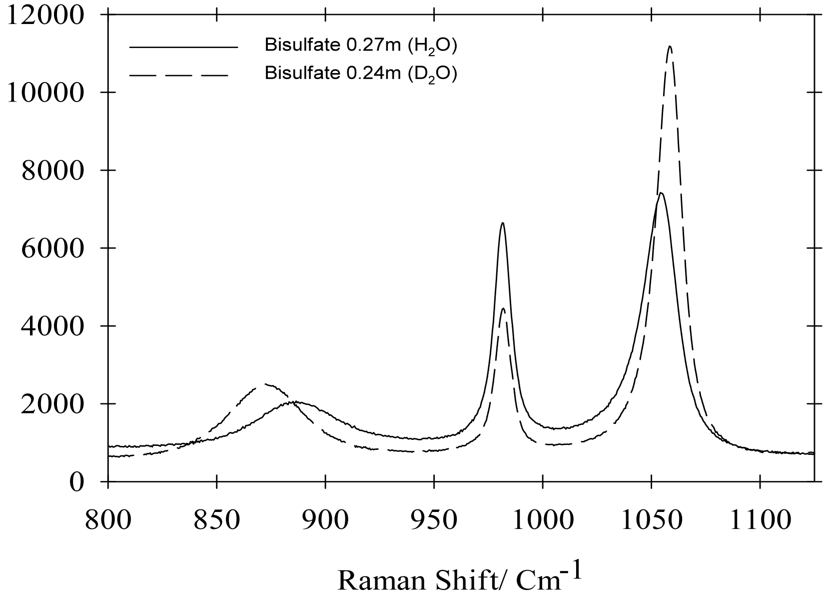

Figure 11 Bisulfate in light and heavy water at 80 °C

4. Phosphoric Acid and Trisodium Phosphate (TSP) Spectra

The first (K_1) and third (K_3) phosphoric acid equilibrium is defined by the following relationships:

$$H_3PO_4 \overset{K_1}{\rightleftharpoons} H^+ + H_2PO_4^- \qquad (16)$$

While the trisodium phosphate equation is:

$$HPO_4^{2-} \overset{K_3}{\rightleftharpoons} H^+ + PO_4^{3-} \qquad (17)$$

Raman spectra for H_3PO_4 and Na_3PO_4 have been measured and are shown in Figures 12 and 13. We are currently working on calculations for the ΔpK values at elevated temperatures at this time.

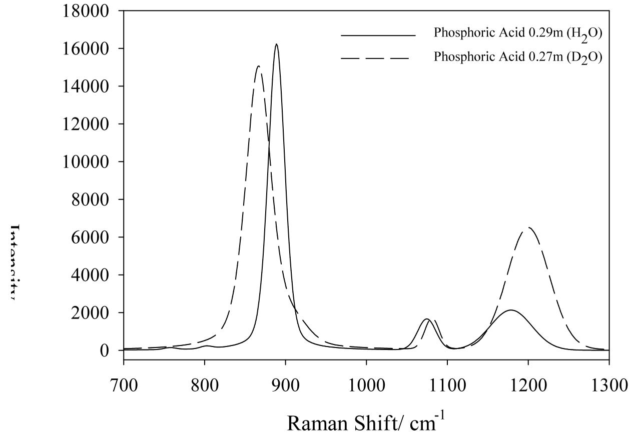

Figure 12 Phosphoric acid spectra in light and heavy water at 25 ^{o}C

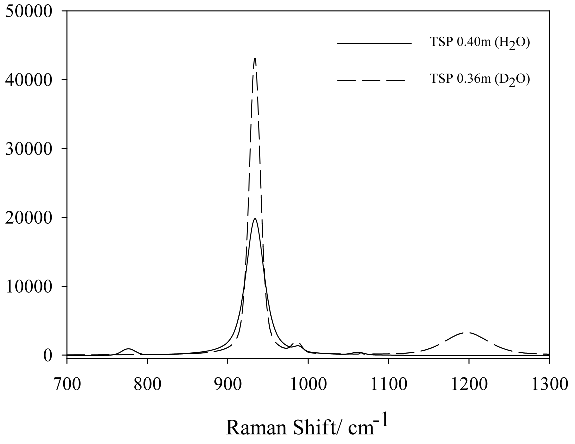

Figure 13 Trisodium phosphate spectra in light and heavy water

5. Conclusion

ΔpK values have been measured for the bisulfate equilibria up to 80 ^{o}C using isotropic Raman spectroscopy. The results for ΔpK with the activity coefficients assumed equal in light and heavy water are 0.35, 0.38 and 0.36 for temperatures of 5 ^{o}C, 25 ^{o}C and 80 ^{o}C, respectively. Further corrections have to be made to incorporate the activity as the assumption of equal activity between light and heavy water are not equal. We are now currently working on the measurements of ΔpK values for the first and third dissociation constant of phosphoric acid.

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