RAMAN AND INFRARED SPECTROSCOPIC INVESTIGATIONS OF AQUEOUS ALKALI METAL PHOSPHATE (PO_4^{3-}) SOLUTIONS

W. W. Rudolph[1*] and G. Irmer[2]

[1]Institut für Virologie im MTZ, TU Dresden, Fetscherstr. 42, D-01307 Dresden, Germany; E-Mail: wolfram.rudolph@mailbox.tu-dresden.de
[2]Institut für theoretische Physik, TU Mining Academy Freiberg, Bernhard v. Cotta Str. 5, D-09596 Freiberg, Germany; E-Mail: gertirmer@physik.tu-freiberg.de

Abstract: Raman and infrared spectra on aqueous Na_3PO_4, and K_3PO_4 solutions have been measured. The modes of the PO_4^{3-} species have been assigned on the basis of T_d symmetry. The pK_3 value of phosphoric acid has been determined by Raman spectroscopy. In addition *ab initio* calculations have been carried out on phosphate and phosphate-water clusters.

Aqueous solutions of Na_3PO_4 (0.0060 – 0.592 mol/L) - and K_3PO_4 (0.0148 – 3.690 mol/L) solutions have been re-investigated by Raman and infrared spectroscopy. It is shown that earlier results are in many respects inadequate (band positions, depolarization degrees etc.) due to the use of non-stoichiometric products or carbonate-contaminated solutions [1, 2]. Although the phosphate ion should have a simple spectrum, there is much confusion in the literature over the assignment of the modes [3, 4]. The "free" phosphate ion, PO_4^{3-}, possesses tetrahedral symmetry (T_d) and has nine normal modes which span the vibrational representation $\Gamma_v(T_d) = a_1 + e + 2f_2$. All modes are Raman active ($\rho(a_1) = 0$; $\rho(e) = \rho(f_2) = \frac{3}{4}$), but only the f modes are infrared allowed.

The four Raman active modes and the two infrared active modes have been assigned as follows: $\nu_2(e) = 414 \pm 2$ cm^{-1}, $\nu_4(f_2) = 558 \pm 2$ cm^{-1} (both depolarized), $\nu_1(a_1) = 936.4 \pm 0.2$ cm^{-1} ($\rho = 0.001$), and $\nu_3(f_2) = 1006 \pm 2$ cm^{-1} (depolarized). The peak position and full width at half height (fwhh) of ν_1 PO_4^{3-} are concentration dependent: in K_3PO_4 solutions shifts the peak position with concentration to slightly lower wavenumbers [4]. The two infrared-active f modes coincide in their peak position with the Raman modes as predicted.

Substitution of water with heavy water causes a shift of ν_1 PO_4^{3-} to 933.5 ± 0.2 cm^{-1}, whilst $\nu_3(f_2)$ shifts to = 1000 ± 2 cm^{-1} [4]. This, and the strong influence on the OD and OH mode, is a clear indication of strong hydrogen bonding, P-O…D(H) (cf. [4, 5]).

Phosphate hydrolyses according to eq. (1): $PO_4^{3-} + H_2O \leftrightarrow HPO_4^{2-} + OH^-$ \hfill (1).

The strongest mode of the HPO_4^{2-} at 990 cm^{-1}, $\nu_1(a_1)$ increases with dilution until it becomes the strongest mode in the Raman spectrum (cf. Figure 1).

In the most concentrated K_3PO_4 solution (mol ratio of salt : H_2O = 1 : 12), the tetrahedral symmetry of PO_4^{3-} is disturbed and the ν_1 mode becomes infrared active. In the supercooled hydrate melt (salt : H_2O = 1 : 8), a low –frequency asymmetry of the ν_1 mode has been noticed [4]. The water content for the most concentrated solution and the melt is not sufficient to hydrate all the ions, and the formation of contact ion pairs is possible.

The quantitative Raman spectroscopic determination of the hydrolysis degree, α, and the determination of pK_3 of the phosphoric acid in these aqueous Na_3PO_4- and K_3PO_4- solutions has been undertaken [4]. The hydrolysis of PO_4^{3-} in aqueous solution may be written according to eq.

(2): $K_h = \dfrac{a_{HPO_4^{2-}} \cdot a_{OH^-}}{a_{PO_4^{3-}}} = \dfrac{[HPO_4^{2-}] \cdot [OH^-]}{[PO_4^{3-}]} \cdot \dfrac{f_{HPO_4^{2-}} \cdot f_{OH^-}}{f_{PO_4^{3-}}} = Q_h \cdot Q_f$ \hfill (2),

with $\quad Q_h = \dfrac{\left[HPO_4^{2-}\right]\cdot\left[OH^-\right]}{\left[PO_4^{3-}\right]} \quad$ and because $[HPO_4^{2-}] = [OH^-]$ it follows $Q_h = \dfrac{\left[HPO_4^{2-}\right]^2}{\left[PO_4^{3-}\right]}$ (3).

The hydrolysis degree α is defined as $\alpha = [HPO_4^{2-}]/C_0$ with C_0 the stoichiometric Na_3PO_4 concentration. For $Q_h = \alpha^2/(1-\alpha)\cdot C_0$. The equilibrium concentration, $[HPO_4^{2-}]$, has been determined by Raman spectroscopy using the $(\nu_1 HPO_4^{2-})$ mode at 990 cm^{-1}. The equilibrium concentration $[PO_4^{3-}]$ follows from $C_0 - [HPO_4^{2-}]$. Q_3, the third equilibrium concentration quotient may be calculated from: $Q_3 = K_W/Q_h$, where K_W = ion product of water. Extrapolation of Q_3 to $C_0 \to 0$ leads to $pK_3 = 12.45 \pm 0.02$ (at 22 °C) in good correspondence with values obtained by traditional thermodynamic procedures [6].

Ab initio molecular orbital simulations for the unhydrated PO_4^{3-} and phosphate–water clusters (with up to 6 water molecules) have been performed and the geometries, energies and vibrational spectra were calculated up to MP2-6-31G(d) [3]. These properties (geometry, energies and vibrational spectra) as a function of increasing cluster size have been studied and the experimental and theoretical spectra are compared.
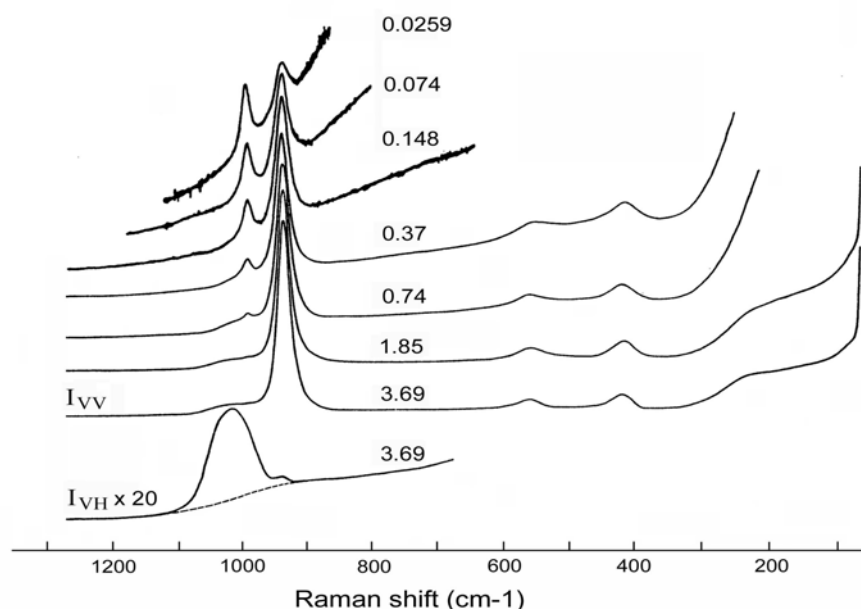

Figure 1: Raman spectra (I_{VV}) of seven aqueous K_3PO_4 solutions in the concentration range from 0.0259 – 3.690 mol/L at 22 °C. For the 3.690 mol/L solution, I_{VH} (x 20) is also shown.

References:
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