

# Raman- and infrared-spectroscopic investigations of dilute aqueous phosphoric acid solutions†

Wolfram W. Rudolph\*

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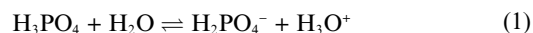
Phosphoric acid in water and heavy water has been studied by Raman and infrared spectroscopy over a broad concentration range (0.00873–1.560 mol kg<sup>-1</sup>) at 23 °C. The vibrational modes of the PO<sub>4</sub> skeleton (C<sub>3v</sub> symmetry) of H<sub>3</sub>PO<sub>4</sub>(aq) and D<sub>3</sub>PO<sub>4</sub>(D<sub>2</sub>O) have been assigned. In addition to the P–O stretching modes a deformation mode has been detected, δPO–H(D) at 1250 and 935 cm<sup>-1</sup>, respectively. In addition to the modes of the phosphoric acid and heavy phosphoric acid a mode of the dissociation product H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and D<sub>2</sub>PO<sub>4</sub><sup>-</sup> has been detected at 1077 cm<sup>-1</sup> and 1084 cm<sup>-1</sup> respectively. H<sub>3</sub>PO<sub>4</sub> and D<sub>3</sub>PO<sub>4</sub> is hydrated in aqueous solution which could be verified by Raman spectroscopy following the νP=O and ν<sub>s</sub>P(OH)<sub>3</sub> mode as a function of temperature. These modes show a pronounced temperature dependence inasmuch as νP=O shifts to higher wavenumbers with temperature increase and ν<sub>s</sub>P(OH)<sub>3</sub> to lower wavenumbers. In the range between 300–600 cm<sup>-1</sup> the deformation modes have been observed. In very dilute H<sub>3</sub>PO<sub>4</sub> solutions however, the dissociation product is the dominant species. The dissociation degree, α for H<sub>3</sub>PO<sub>4</sub>(aq) and D<sub>3</sub>PO<sub>4</sub>(D<sub>2</sub>O) as a function of dilution has been measured at 23 °C. In these dilute H<sub>3</sub>PO<sub>4</sub>(aq) and D<sub>3</sub>PO<sub>4</sub>(D<sub>2</sub>O) solutions no spectroscopic features for a dimeric species of the formula H<sub>6</sub>P<sub>2</sub>O<sub>8</sub> and D<sub>6</sub>P<sub>2</sub>O<sub>8</sub> could be detected. Quantitative Raman measurements have been carried out to follow the dissociation of H<sub>3</sub>PO<sub>4</sub> and D<sub>3</sub>PO<sub>4</sub> over a very broad concentration range and also as a function of temperature. From the dissociation data, the pK<sub>1</sub> value for H<sub>3</sub>PO<sub>4</sub> has been determined to 2.14(1) and for D<sub>3</sub>PO<sub>4</sub> to 2.42(1) at 23 °C. In the temperature interval from 24.5 to 99.7 °C the pK<sub>1</sub> values for H<sub>3</sub>PO<sub>4</sub>(aq) have been determined and thermodynamic data have been derived.

## 1. Introduction

Unquestionably, the industrial<sup>1</sup> and biological importance<sup>2,3</sup> of phosphate systems brought about extensive investigations of physicochemical properties of aqueous solutions of phosphoric acid and phosphates. Among many techniques, Raman and infrared spectroscopy has been used quite extensively.<sup>4–13</sup> The spectroscopic material published however, showed disagreement concerning the peak positions of the fundamental modes, depolarization degrees, and other band parameters. In some cases, the number of modes contradicted the predicted ones deduced from group theory for H<sub>3</sub>PO<sub>4</sub>. Although the phosphoric acid should have a simple spectrum, there is much confusion in the literature over the assignment of the modes. In a standard work<sup>14</sup> and earlier publications<sup>4–7</sup> the modes of the H<sub>3</sub>PO<sub>4</sub>(aq) were confused with the modes of its dissociation product H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq).

Simultaneous to these vibrational studies, a number of investigations on phosphoric acid solutions were done using methods such as potentiometry, conductivity, ultrasonic absorption and vapour pressure measurements. The main purpose concerned the determination of the dissociation of the phosphoric acid and therefore raised questions concerning the nature of the species

present.<sup>15–33</sup> The first dissociation equilibrium of the phosphoric acid:



is well known from thermodynamic studies and from conductivity work at room temperature<sup>16,19,22</sup> and have also been extended to higher temperatures and pressures.<sup>26,31</sup> From a number of these studies, the structure of the species has been proposed and dimeric species such as H<sub>6</sub>P<sub>2</sub>O<sub>6</sub> and H<sub>5</sub>P<sub>2</sub>O<sub>6</sub><sup>-</sup> have been deduced<sup>20,21,28</sup> while others denied the need to invoke such species.<sup>16,22,26,30</sup>

The structure of phosphoric acid in aqueous solution has been obtained by an earlier X – ray diffraction study<sup>34</sup> on two concentrated aqueous H<sub>3</sub>PO<sub>4</sub> solutions. A peak in the range ~3.75 Å in the correlation functions revealed the presence of H<sub>3</sub>PO<sub>4</sub>–H<sub>2</sub>O interactions and each H<sub>3</sub>PO<sub>4</sub> molecule interacts with about four water molecules. The existence of a hydration shell around H<sub>3</sub>PO<sub>4</sub> in aqueous solution had been inferred from earlier diffusion measurements.<sup>15</sup> A recent neutron diffraction and isotopic substitution study (NDIS)<sup>35</sup> was applied on hydrogen phosphate solutions and showed the existence of strong hydrogen bonds formed between phosphate anions and water molecules and a hydration number of 11–15 was found. Density functional theory/molecular dynamics simulation<sup>36</sup> of aqueous solutions of orthophosphate species H<sub>n</sub>PO<sub>4</sub><sup>3-n</sup> (n = 0–3) provided insights into hydrogen transfer and hydration properties of these aqueous species. A first hydration shell of PO<sub>4</sub><sup>3-</sup>, HPO<sub>4</sub><sup>2-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> displayed a flexible first coordination shell between 13 and 7 water molecules decreasing from PO<sub>4</sub><sup>3-</sup> to H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. The H-bond

Institut für Virologie im MTZ, TU Dresden, Fetscherstr. 74, D-01307, Dresden, Germany. E-mail: wolfram.rudolph@tu-dresden.de

† Electronic supplementary information (ESI) available: Geometry of the H<sub>3</sub>PO<sub>4</sub> molecules (C<sub>3</sub> symmetry) and the numbering of the atoms which is used for the definition of the parameters in Table 2. See DOI: 10.1039/c0dt00417k

interactions between the oxygen atoms of the phosphates and the surrounding water molecules explained the diminished effect on the structure of water with increasing hydrogenation of the orthophosphates. A computer simulation on aqueous  $K_3PO_4$ ,  $K_2HPO_4$ , and  $KH_2PO_4$  solutions<sup>37</sup> confirmed the strong hydration effect of these ions and a partially ordered second hydration shell.

Raman and infrared spectroscopic techniques are well suited for studying the structural aspect of the species present as well as allowing quantification of the first dissociation step. In recent publications from our laboratory<sup>9–12</sup> the structure, vibrational spectra and dissociation of aqueous phosphoric acid solutions at room temperature have been partially reported. From these studies it became clear that the phosphoric acid is quite strongly hydrated. Due to the strong hydration the characteristic modes of the P=O group and the P(OH)<sub>3</sub> group are influenced resulting in a shift of the characteristic modes compared to the ones in  $H_3PO_4$  systems in non-polar solvents. It could be shown that the overlap with the modes of  $H_2PO_4^-(aq)$ , the dissociation product of phosphoric acid caused many erroneous interpretations of both the vibrational spectrum and the definition of the symmetry of the  $PO_4$  unit (*cf. e.g. ref.[11]*). The present investigation builds not only on earlier results but also provides vibrational data on dilute aqueous solutions of phosphoric acid. In addition deuterated phosphoric acid was studied. In order to study the hydration on  $H_3PO_4$  in aqueous solution concentrations were measured to very dilute solutions and also as function of temperature. Quantitative measurements have also been carried out to determine the first dissociation constant as a function of dilution, of added neutral salt and change in temperature.

## 2. Experimental section

Commercial phosphoric acid contains traces of fluorescing substances and therefore the phosphoric acid has been prepared with sublimated  $P_4O_{10}$  in order to achieve high quality Raman spectra. The  $P_4O_{10}$  has been sublimated in a home built sublimation apparatus and then the  $P_4O_{10}$  converted with ultrapure water (PureLab Plus, Ultra-pure Water Purification Systems) in a moisturizing apparatus according to reaction (2):



The stock solution was filtered through a G5 sintered-glass frit (Schott & Genossen, Jena) under  $CO_2$  free atmosphere. A stock solution was prepared with a concentration of  $1.450 \text{ mol L}^{-1}$  ( $\rho = 1.0713 \text{ g cm}^{-3}$  at  $23 \text{ }^\circ\text{C}$ ) equal to  $1.5604 \text{ mol kg}^{-1}$ . The lower concentrated  $H_3PO_4$  solutions were prepared with ultrapure water free of  $CO_2$  by weight. A  $D_3PO_4$  stock solution,  $1.430 \text{ mol L}^{-1}$  ( $1.1712 \text{ g cm}^{-3}$  at  $23 \text{ }^\circ\text{C}$ ) equal to  $1.390 \text{ mol kg}^{-1}$  has been prepared according to the above described procedure but using  $D_2O$  (Merck Chemicals, 99.9% D) instead of water. The lower concentrated  $D_3PO_4$  solutions were prepared with  $D_2O$  by weight. For further details on the preparation of  $H_3PO_4$  and  $D_3PO_4$  *cf. ref. [11,12]*.

The phosphate content of the stock solution was determined by gravimetry.<sup>38</sup> The solution densities were determined with a pycnometer of 5.000 mL volume at  $(23 \pm 0.1) \text{ }^\circ\text{C}$ .

$NaH_2PO_4$  and  $KH_2PO_4$  solutions have been prepared with ultrapure water free of  $CO_2$  by weight. The solution densities

were determined with a pycnometer of 5.000 mL volume at  $(23 \pm 0.1) \text{ }^\circ\text{C}$ .<sup>11,12</sup>

### Raman and IR spectroscopic measurements<sup>39,40</sup>

Raman spectra were measured with equipment at the TU Dresden<sup>39</sup> at  $(23 \pm 0.1) \text{ }^\circ\text{C}$ . The spectra were excited with the 487.98 nm of an  $Ar^+$  laser at power levels  $\sim 1200 \text{ mW}$ . After passing the Zeiss double monochromator GDM 1000, with gratings of 1300 grooves/mm, the scattered light was detected with a cooled photo multiplier tube ITT 130 in the photon counting mode. A scrambler in front of the slit served to compensate for grating preference.  $I_{VV}$  and  $I_{VH}$  spectra were obtained with fixed polarisation of the laser beam by changing the polarisation filter (Bernotar foil) in the parallel and perpendicular arrangement between the sample and the entrance slit to give the scattering geometries:

$$I_{VV} = I(Y[ZZ]X) = 45\alpha^2 + 4\gamma^2 \quad (3)$$

$$I_{VH} = I(Y[ZY]X) = 3\gamma^2 \quad (4)$$

The isotropic spectrum,  $I_{iso}$  or  $I_\alpha$  was then constructed:

$$I_{iso} = I_{VV} - 4/3 \cdot I_{VH} \quad (5)$$

The depolarization ratio,  $\rho$ , of the modes has been determined according to eqn (6):

$$\rho = I_{VH}/I_{VV} = 3\gamma^2/(45\alpha^2 + 4\gamma^2) \quad (6)$$

The polarization analyser has been calibrated with  $CCl_4$  before each measuring cycle and adjusted if necessary. The depolarisation ratio of the  $\nu_1$  mode of  $CCl_4$  at  $459 \text{ cm}^{-1}$  has been measured 15 times and a depolarization ratio equal to  $0.0036 \pm 0.0005$  determined. The depolarization ratio of the  $CCl_4$  modes at 217 and  $315 \text{ cm}^{-1}$  (these modes are depolarised according to the theory) have been determined to  $0.75 \pm 0.02$ .

A second set of Raman spectra were measured in the macro chamber of the T 64000 Raman spectrometer from Jobin Yvon in a  $90^\circ$  scattering geometry at  $(23 \pm 0.1) \text{ }^\circ\text{C}$ . The spectra were excited with the 487.98 nm line of an  $Ar^+$  laser at a power level of  $\sim 1100 \text{ mW}$  at the sample. After passing the spectrometer in subtractive mode, with gratings of 1800 grooves/mm, the scattered light was detected with a cooled CCD detector. A more detailed description of the Raman measurements is given in ref.40

### Quantitative Raman measurements

Quantitative Raman measurements have been carried out to determine the first dissociation constant of phosphoric acid according to an external quantification method previously described<sup>11</sup> Raman spectra were measured with equipment at the TU Dresden<sup>39</sup> at  $(23 \pm 0.1) \text{ }^\circ\text{C}$  and  $\sim 1.5 \text{ mL}$  solutions have been measured in  $3.5 \text{ mL}$  quartz cuvette with a tightly fitted Teflon stopper from Hellma, Müllheim/Baden, Germany (path length 10 mm). The spectra were excited with the 487.98 nm of an  $Ar^+$  laser at power levels  $\sim 1200 \text{ mW}$  at the sample and only the  $I_{VV}$  scattering has been recorded. The stability of the apparatus has been checked, including the laser power, by measuring the  $\nu_1$  mode of  $SO_4^{2-}$  of a  $0.740 \text{ mol L}^{-1}$   $K_2SO_4$  solution during the measuring cycle of  $\sim 1.5 \text{ h}$ . The variation of the integrated band intensity of the external

reference mode  $\nu_1\text{SO}_4^{2-}$  at  $981\text{ cm}^{-1}$  was better than  $\pm 1\%$  during a measuring cycle. The analytical band of  $\text{H}_2\text{PO}_4^-(\text{aq})$  the mode at  $1077\text{ cm}^{-1}$ ,  $\nu_3\text{PO}_2$  has been chosen because it is the strongest Raman mode of  $\text{H}_2\text{PO}_4^-(\text{aq})$ , and furthermore this mode does not overlap with modes of  $\text{H}_3\text{PO}_4(\text{aq})$  and were integrated after subtracting a synthetic baseline in the wavenumber limits from  $1025\text{--}1128\text{ cm}^{-1}$ . Great care was taken to measure high quality spectra. The signal to noise ratio (S/N ratio) of the spectra of a  $0.183\text{ mol kg}^{-1}$   $\text{H}_3\text{PO}_4$  solution has been determined to  $\sim 940$ . The S/N ratio for the lower concentrated solutions dropped and for a solution  $0.0124\text{ mol kg}^{-1}$  a value of  $\sim 180$  has been reached. Twelve  $\text{NaH}_2\text{PO}_4$  solutions ( $0.00696\text{--}0.870\text{ mol kg}^{-1}$ ) have been measured in the wavenumber range from  $780\text{--}1280\text{ cm}^{-1}$  and 12 solutions of  $\text{H}_3\text{PO}_4(\text{aq})$  ( $0.00873\text{--}0.2515\text{ mol kg}^{-1}$ ). The measuring cycle was as follows: first, measurement of the  $\text{H}_3\text{PO}_4$  solution, second, the  $\text{SO}_4^{2-}(\text{aq})$  and then the  $\text{NaH}_2\text{PO}_4$  solution and so forth. Two independent measuring series have been carried out for the  $\text{NaH}_2\text{PO}_4^-$  and  $\text{H}_3\text{PO}_4^-$  solutions. The integrated band intensity,  $A_{1077}$  as a function of concentration has been determined and from this calibration curve the equilibrium concentration of  $\text{H}_2\text{PO}_4^-$ ,  $[\text{H}_2\text{PO}_4^-]$  determined in the phosphoric acid solutions ( $A_{1077} = 63.0297 \cdot m_{\text{H}_2\text{PO}_4^-}$ ;  $R^2 = 0.9996$ ). An identical procedure has been employed for  $\text{NaD}_2\text{PO}_4^-$  and  $\text{D}_3\text{PO}_4$  solutions ( $0.00644\text{--}0.5293\text{ mol kg}^{-1}$ ). The integrated band intensity,  $A_{1084}$  as a function of  $\text{NaD}_2\text{PO}_4$  concentration ( $0.00505\text{--}0.0505\text{ mol kg}^{-1}$ ; 11 solutions) was plotted and from this linear calibration curve of  $\text{D}_2\text{PO}_4^-$ ,  $[\text{D}_2\text{PO}_4^-]$  has been determined ( $A_{1084} = 77.6237 \cdot m_{\text{D}_2\text{PO}_4^-}$ ;  $R^2 = 0.9990$ ). (The equilibrium species concentration  $i$  is denoted as [i].)

The Raman temperature measurements have been carried out in a home built Raman oven similar to the one described in ref. [41]. The  $\text{H}_3\text{PO}_4$  solutions have been sealed in quartz tubes and only the  $I_{\text{VV}}$ -scattering has been measured. The quantification has been carried out according to a previously described external reference method.<sup>11,12</sup> Briefly, for a  $0.2515\text{ mol kg}^{-1}$  ( $0.248\text{ mol L}^{-1}$ )  $\text{H}_3\text{PO}_4$  solution, the equilibrium concentration of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$  were obtained from the ratios of the integrated band areas of the  $1178\text{ cm}^{-1}$  mode of  $\text{H}_3\text{PO}_4$  ( $\nu\text{P}=\text{O}$ ) and the  $1077\text{ cm}^{-1}$  mode of  $\text{H}_2\text{PO}_4^-$  ( $\nu_3\text{PO}_2$ ). The  $J$ -value of the band at  $1077\text{ cm}^{-1}$  of the species  $\text{H}_2\text{PO}_4^-$  has been determined for three  $\text{NaH}_2\text{PO}_4$  solutions with known amounts of perchlorate as internal standard ( $\text{NaClO}_4$ ). Similarly, the  $J$ -value of the band at  $1178\text{ cm}^{-1}$  of  $\text{H}_3\text{PO}_4$  has been determined in three  $\text{H}_3\text{PO}_4$  solutions with additional  $\text{HCl}$  (suppression of dissociation) and  $\text{ClO}_4^-$  as internal standard.  $\text{NaClO}_4$  has been used as internal standard substance in both cases. The relative molar scattering factors for these modes,  $J_{1178}$  and  $J_{1077}$  are equal to  $0.340$  and  $1.000$  respectively. The sum of the equilibrium concentrations  $[\text{H}_3\text{PO}_4]$  and  $[\text{H}_2\text{PO}_4^-]$  is equal to  $m_{\text{T}}$ , the stoichiometric concentration of  $\text{H}_3\text{PO}_4$  (in  $\text{mol kg}^{-1}$ ):

$$m_{\text{T}} = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] \quad (7)$$

Furthermore, the integrated band intensities for the  $\text{H}_3\text{PO}_4$  mode at  $1178\text{ cm}^{-1}$  and the  $\text{H}_2\text{PO}_4^-$  mode at  $1077\text{ cm}^{-1}$  can be expressed as follows:  $A_{1178} = J_{1178} [\text{H}_3\text{PO}_4]$  and  $A_{1077} = J_{1077} [\text{H}_2\text{PO}_4^-]$ . The ratio of the integrated intensities,  $A_{1077}/A_{1178}$  was calculated:

$$\frac{A_{1077}}{A_{1078}} = \frac{[\text{H}_2\text{PO}_4^-] \cdot J_{1077}}{[\text{H}_2\text{PO}_4^-] \cdot J_{1078}} \quad (8)$$

After rearranging eqn (8) for  $[\text{H}_2\text{PO}_4^-]$  it follows:

$$[\text{H}_2\text{PO}_4^-] = \frac{A_{1077} \cdot J_{1178}}{A_{1178} \cdot J_{1077}} \quad (9)$$

In the  $I_{\text{VV}}$  scattering the  $\text{H}_3\text{PO}_4$  band at  $1178$  has a slight intensity contribution from the band at  $1160\text{ cm}^{-1}$  of the dissociation product  $\text{H}_2\text{PO}_4^-$ , namely  $\nu_{\text{as}}\text{PO}_2$  (cf. ref. [11]). The band  $\nu_{\text{as}}\text{PO}_2$  is of much lower intensity than  $\nu_3\text{PO}_2$  and the intensity ratio  $J_{1077}/J_{1160} = 34/1$  and the corrected band intensity,  $A_{1178}$  may be expressed as follows:  $A_{1178} = A_{1178}^* - 0.029 \cdot A_{1077}$  and substituting this expression into eqn (9) it follows:

$$[\text{H}_2\text{PO}_4^-] = \frac{A_{1077} \cdot J_{1178}}{(A_{1178}^* - 0.029 \cdot A_{1077}) \cdot J_{1077}} \quad (10)$$

with  $A_{1178}^*$  as the uncorrected integrated band intensity of the mode at  $1178\text{ cm}^{-1}$ . With the equilibrium concentration of  $\text{H}_2\text{PO}_4^-$  on hand and  $m_{\text{T}}$ , the stoichiometric solute concentration known, the hydrolysis degree,  $\alpha$  in  $\text{H}_3\text{PO}_4(\text{aq})$  is defined as:

$$\alpha = [\text{H}_2\text{PO}_4^-]/m_{\text{T}} \quad (11)$$

and it follows therefore  $[\text{H}_2\text{PO}_4^-] = \alpha \cdot m_{\text{T}}$ .

### FT-IR- measurements

Infrared (IR) solution spectra were measured between  $400\text{--}4000\text{ cm}^{-1}$  with a FTIR spectrometer described in refs. [11,40] between KBr disks protected with a thin ( $20\text{ }\mu\text{m}$ ) polyethylene (PE) film. The thin PE-film protects the KBr windows and is easily subtracted from the measured spectrum.

### Density Fuctional Theory calculations

The optimization of the molecular geometry and the calculation of the vibrational spectra was performed with the Density Functional Theory (DFT) method B3LYP using the basis set B3LYP 6-311+G(3d,f) using Gaussian 03.<sup>52</sup> The optimization procedure led to a stable configuration with  $C_3$  symmetry and no imaginary frequencies appeared. Calculations have been carried out on the single  $\text{H}_3\text{PO}_4$  molecule *in vacuo* and in the presence of the solvent (water) by placing  $\text{H}_3\text{PO}_4$  within the solvent reaction field. The Polarized Continuum Model (PCM) creates the solute cavity *via* a set of interlocking spheres centred on the atoms, and uses a numerical representation of the polarization of the solvent (ref. 53).

## 3. Results and discussions

### 3.1. Raman and infrared spectra of dilute $\text{H}_3\text{PO}_4$ and $\text{D}_3\text{PO}_4$

In the gas phase the  $\text{H}_3\text{PO}_4$  molecule possesses  $C_3$  symmetry according to DFT calculations and a detailed account of the data will be presented in a forthcoming paper.<sup>42</sup> The wavenumber positions for the  $\text{H}_3\text{PO}_4$  molecule *in vacuo* are presented in Table 1 and for  $\text{H}_3\text{PO}_4$  with an explicit solvation shell (hydration shell) in Table 2. The geometry parameters of the  $\text{H}_3\text{PO}_4$  *in vacuo* and  $\text{H}_3\text{PO}_4$  with solvation,  $\text{H}_3\text{PO}_4(\text{aq})$ , are presented in Table 3 and in Figure S1† the structure and the numbering of the atoms is given. These DFT results will be discussed after the discussion of the measured vibrational data.

**Table 1** DFT Raman and infrared data for H<sub>3</sub>PO<sub>4</sub> in the gas phase

$\tilde{\nu}_{\max}/\text{cm}^{-1}$	Raman		Character	Intensity IR	Normal modes
	Intensity	Depol. degree			
157.9	1.3	0.75	e	69.0	$\rho\text{OH}$
310.4	0.2	0.02	a	87.7	$\rho\text{OH}$
376.1	0.8	0.75	e	42.0	$\rho\text{OH} + \delta\text{OPO}$
454.2	0.8	0.60	a	14.5	$\delta_{\text{as}}\text{OPO}$
458.4	1.8	0.75	e	64.5	$\delta_{\text{as}}\text{OPO}$
839.4	21.1	0	a	19.7	$\nu_{\text{s}}\text{P}(\text{OH})_3$
919.8	1.4	0.75	e	335.1	$\nu_{\text{as}}\text{P}(\text{OH})_3$
1053.9	1.6	0.75	a	93.7	$\delta\text{POH}$
1064.1	1.3	0.75	e	54.6	$\delta\text{POH}$
1318.4	9.7	0.11	a	316.4	$\nu\text{P}=\text{O}$
3821.7	34.6	0.75	e	173.2	$\nu_{\text{as}}\text{OH}$
3824.0	126.3	0.05	a	21.3	$\nu_{\text{s}}\text{OH}$

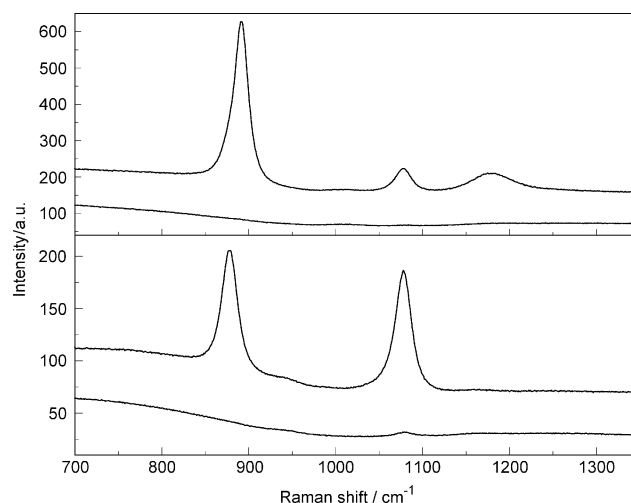
**Table 2** DFT Raman and infrared data for H<sub>3</sub>PO<sub>4</sub> with solvation shell

$\tilde{\nu}_{\max}/\text{cm}^{-1}$	Raman		Character	IR Intensity	Normal modes
	Intensity	Depol. degree			
175.1	1.9	0.75	e	166.5	$\rho\text{OH}$
322.3	0.1	0.02	a	237.0	$\rho\text{OH}$
363.9	1.6	0.75	e	71.5	$\rho\text{OH} + \delta\text{OPO}$
452.1	3.6	0.75	e	107.2	$\delta_{\text{as}}\text{OPO}$
459.2	1.8	0.65	a	20.6	$\delta_{\text{s}}\text{OPO}$
849.8	40.9	0	a	32.9	$\nu_{\text{s}}\text{P}(\text{OH})_3$
898.0	2.1	0.75	e	506.9	$\nu_{\text{as}}\text{P}(\text{OH})_3$
993.4	2.1	0.71	a	234.2	$\delta\text{POH}$
1026.3	2.6	0.75	e	92.0	$\delta\text{POH}$
1245.8	21.9	0.11	a	526.8	$\nu\text{P}=\text{O}$
3274.3	60.7	0.75	e	726.0	$\nu_{\text{as}}\text{OH}$
3293.5	338.9	0.04	a	77.3	$\nu_{\text{s}}\text{OH}$

**Table 3** Geometrical parameters for H<sub>3</sub>PO<sub>4</sub> in gas phase and with solvation sphere (symmetry C<sub>3v</sub>)

Parameter	Molecule in gas phase	Molecule with solvation shell
a <sub>12</sub> ; P=O b. length	1.463	1.474
a <sub>13</sub> ; P-O b. length	1.590	1.582
a <sub>56</sub> ; O-H b. length	0.964	0.989
$\alpha_{156}$ ; angle P-O-H	112.5°	113.7°
$\alpha_{315}$ ; angle O-P-O	102.0°	102.6°
$\alpha_{215}$ ; angle O=P-O	116.2°	115.7°
d <sub>2138</sub> ; dihedral angle	33.5°	39.3°
W (a.u.)	-644.33557540	-644.37647586

The PO<sub>4</sub> unit of the molecule of the isolated H<sub>3</sub>PO<sub>4</sub> molecule possesses C<sub>3v</sub> symmetry considering the OH groups as point masses. In solution, such an assumption seems reasonable because the normal modes of PO-H such as  $\nu\text{OH}$ ,  $\delta\text{PO-H}$ , and  $\gamma\text{PO-H}$  are mostly decoupled from the O=PO<sub>3</sub> skeleton modes. The O=PO<sub>3</sub> skeleton has 5 atoms which corresponds to 9 normal modes (n.m.). The irreducible representation of the vibrational modes is as follows:  $\Gamma_{\text{vib}}(C_{3v}) = 3a_1(\text{Ra, i.r.}) + 3e(\text{Ra, i.r.})$ . All the modes with the character a<sub>1</sub>, and e are Raman active and infrared allowed. The modes with the character a are:  $\nu_1(a_1) = \nu_{\text{s}}\text{P}(\text{OH})_3$ ,  $\nu_2(a_1) = \nu\text{P}=\text{O}$  and  $\nu_3(a_1) = \delta_{\text{s}}\text{P}(\text{OH})_3$ . These modes are polarized in the Raman effect. The modes  $\nu_4(e) = \nu_{\text{as}}\text{P}(\text{OH})_3$ ,  $\nu_5(e) = \delta_{\text{as}}\text{P}(\text{OH})_3$ , and  $\nu_6(e) = \rho\text{OP}(\text{OH})_3$  have the character e and are expected to be depolarized in the Raman effect. The deformation modes of



**Fig. 1** Upper panel: Raman spectrum ( $I_{\text{VV}}$  and  $I_{\text{VH}}$  scattering) of a 0.183 mol kg<sup>-1</sup> (0.181 mol L<sup>-1</sup>) H<sub>3</sub>PO<sub>4</sub>(aq). The modes of H<sub>3</sub>PO<sub>4</sub>(aq) in the P-O stretching region are:  $\nu_{\text{s}}\text{P}(\text{OH})_3$  at 890 cm<sup>-1</sup>,  $\nu_{\text{as}}\text{P}(\text{OH})_3$  at 1008 cm<sup>-1</sup> (very weak), and  $\nu\text{P}=\text{O}$  at 1178 cm<sup>-1</sup>. The very weak, broad mode  $\delta\text{PO-H}$  at 1250 cm<sup>-1</sup> is almost not visible in the Raman effect. Lower panel: Raman spectrum of a 0.112 mol kg<sup>-1</sup> (0.111 mol L<sup>-1</sup>) NaH<sub>2</sub>PO<sub>4</sub> solution at 23 °C. The modes of H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq) in the P-O stretching region are:  $\nu_{\text{s}}\text{P}(\text{OH})_2$  at 877 cm<sup>-1</sup>,  $\nu_{\text{as}}\text{P}(\text{OH})_2$  at 942 cm<sup>-1</sup> (very weak),  $\nu_{\text{s}}\text{PO}_2$  at 1077 cm<sup>-1</sup>, and  $\nu_{\text{as}}\text{PO}_2$  at 1160 cm<sup>-1</sup> (very weak).

the O=PO<sub>3</sub> unit occur below 550 cm<sup>-1</sup> and the P-O stretching modes above 750 cm<sup>-1</sup>. In the older literature the PO<sub>4</sub> group of phosphoric acid has been assigned to contradicting point groups such as T<sub>d</sub><sup>4</sup>, C<sub>2v</sub><sup>6</sup> and also C<sub>3v</sub><sup>8</sup>

Before a more detailed analysis of individual H<sub>3</sub>PO<sub>4</sub> bands are discussed, it is instructive to compare the H<sub>3</sub>PO<sub>4</sub>(aq) spectrum of a 0.183 mol kg<sup>-1</sup> (0.181 mol L<sup>-1</sup>) solution with a spectrum of 0.112 mol kg<sup>-1</sup> (0.111 mol L<sup>-1</sup>) NaH<sub>2</sub>PO<sub>4</sub> solution (Fig. 1). From this comparison it is obvious that with the exception of the very weak mode at 1008 cm<sup>-1</sup>, all other modes in the P-O stretching region of the spectrum (800–1400 cm<sup>-1</sup>) are more or less overlapped with the modes of H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq). The spectral data for a 0.112 mol kg<sup>-1</sup> H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq) are given in Table 4 and in Fig. 1, lower panel, where only the P-O stretching modes are presented.

From this comparison it becomes clear that the band at 1077 cm<sup>-1</sup> in the H<sub>3</sub>PO<sub>4</sub>(aq) spectrum has to be assigned to  $\nu_{\text{s}}\text{PO}_2$  of H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq) the dissociation product according to reaction (1).

**Table 4** Raman data of the PO<sub>4</sub> modes of H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq) in dilute NaH<sub>2</sub>PO<sub>4</sub> solutions at 23 °C

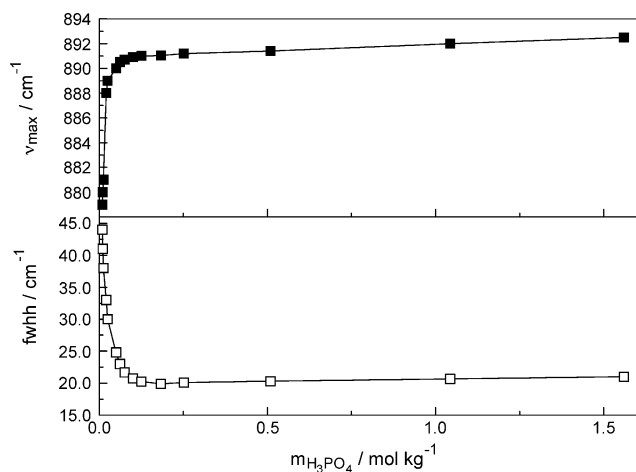
$\tilde{\nu}_{\max}/\text{cm}^{-1}$	Intensity	fwhh cm <sup>-1</sup>	Depolarization degree	Assignment
371*	2	45	0.75	$\rho, \tau, \omega\text{O}_2\text{P}(\text{OH})_2$
393*	3	60	0.75	
515*	3.5	54	0.60	$\delta\text{P}(\text{OH})_2 + \delta\text{PO}_2$
877	100	19.5	0.007	$\nu_{\text{s}}\text{P}(\text{OH})_2$
942	2.94	26	0.75	$\nu_{\text{as}}\text{P}(\text{OH})_2$
1077	89.1	20	0.038	$\nu_{\text{s}}\text{PO}_2$
1160	2.63	26	0.75	$\nu_{\text{as}}\text{PO}_2$
1240 <sup>+</sup>	0.5	40	0.10	$\delta\text{PO-H}$

\*For the C<sub>2v</sub> symmetry of the \*O<sub>2</sub>PO<sub>2</sub> skeleton modes 5 deformation modes are expected; broad double band, depolarized and the broad polarized deformation mode constitute accidental overlapped bands. <sup>+</sup>This very weak broad mode is not observable in dilute solutions



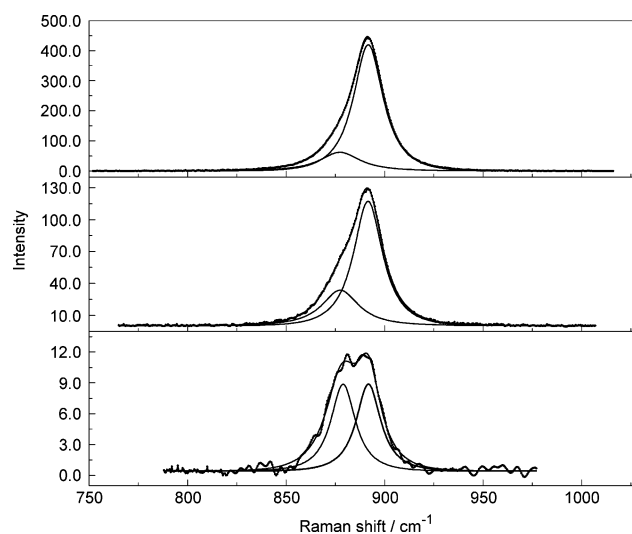
(This mode is also used for analytical purposes; see experimental section.) The other strong band in  $\text{H}_2\text{PO}_4^-(\text{aq})$  spectrum at  $877\text{ cm}^{-1}$  assigned to  $\nu_s\text{P}(\text{OH})_2$  overlaps strongly with the mode of the phosphoric acid at  $890\text{ cm}^{-1}$ . The influence of  $\text{H}_2\text{PO}_4^-(\text{aq})$  on the spectrum of  $\text{H}_3\text{PO}_4(\text{aq})$  has already been established.<sup>11</sup> It had been found that the successive addition of HCl suppresses the band at  $1077\text{ cm}^{-1}$ . In a spectrum of a  $0.310\text{ mol L}^{-1}$   $\text{H}_3\text{PO}_4(\text{aq})$  solution with  $1.44\text{ mol L}^{-1}$  HCl added the mode at  $1077\text{ cm}^{-1}$  had almost completely disappeared and furthermore, the mode at  $890\text{ cm}^{-1}$  becomes symmetrical (see Fig. 1 ref. [11]). The intensity contribution of the  $\text{H}_2\text{PO}_4^-(\text{aq})$  mode at  $877\text{ cm}^{-1}$  and  $\nu_s\text{P}(\text{OH})_3$  of  $\text{H}_3\text{PO}_4(\text{aq})$  at  $890\text{ cm}^{-1}$  overlap almost completely and cannot be separated in a meaningful way. The term “ $890\text{ cm}^{-1}$ ” band has been coined<sup>8</sup> and may express this situation. The peak position ( $\tilde{\nu}_{\text{max}}$ ) and the full width at half height (fwhh) of the “ $890\text{ cm}^{-1}$ ” (sum) band are presented in Fig. 2. The distinct concentration dependence of  $\tilde{\nu}_{\text{max}}$  and of the fwhh are clearly due to the dissociation of  $\text{H}_3\text{PO}_4(\text{aq})$  which is a function of dilution. For a meaningful band separation of these severely overlapped bands ( $877$  and  $890\text{ cm}^{-1}$ ) additional information would be necessary. The intensity of the  $\text{H}_2\text{PO}_4^-(\text{aq})$  mode,  $\nu_s\text{PO}_2$  at  $1077\text{ cm}^{-1}$  however, does not overlap with any of the bands of phosphoric acid. From its known intensity and under consideration of the  $J$ -values for the  $\text{H}_2\text{PO}_4^-(\text{aq})$  bands, the band intensity of the mode at  $877\text{ cm}^{-1}$  may be calculated:  $A_{877} = \frac{J_{1077}}{J_{877}} \cdot A_{1077} = 1.122 \cdot A_{1077}$ .

Representative spectra of dilute phosphoric acid solutions together with the result of the band fit and the component bands at  $877$  and  $890\text{ cm}^{-1}$  are presented in Fig. 3.

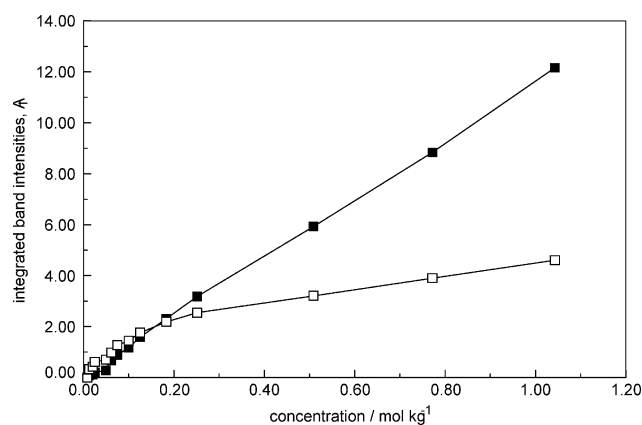


**Fig. 2** Position of the band maximum,  $\nu_{\text{max}}$  (upper panel) and fwhh (lower panel) of the “ $890\text{ cm}^{-1}$ -band” versus the stoichiometric  $\text{H}_3\text{PO}_4$  concentration at  $23\text{ }^\circ\text{C}$ .

Furthermore, the integrated band intensities,  $A_i$  of the mode  $\nu\text{P}=\text{O}$  for  $[\text{H}_3\text{PO}_4]$  at  $1178\text{ cm}^{-1}$  and for  $[\text{H}_2\text{PO}_4^-]$  at  $1077\text{ cm}^{-1}$  versus the stoichiometric phosphoric acid concentration is presented in Fig. 4. The  $A_i$ -value of the mode at  $1178\text{ cm}^{-1}$  of the equilibrium concentration of  $\text{H}_3\text{PO}_4$ ,  $[\text{H}_3\text{PO}_4]$ , rises steadily while  $A_i$  for  $[\text{H}_2\text{PO}_4^-]$  levels off. This behaviour is an expression of the decreasing dissociation degree  $\alpha$  of the phosphoric acid with increasing concentration. The band intensity of the  $\nu\text{P}=\text{O}$  is completely overlapped with a mode of  $\text{H}_2\text{PO}_4^-(\text{aq})$ ,  $\nu_{\text{as}}\text{PO}_2$  at



**Fig. 3** Isotropic Raman spectra of 3 dilute phosphoric acid solutions. From the isotropic spectrum  $I_{\text{iso}}(\text{H}_3\text{PO}_4)$  the background spectrum  $I_{\text{iso}}(\text{H}_2\text{O})$  has been subtracted. Given are the measured, background corrected spectra, the two band components at  $877$  and  $890\text{ cm}^{-1}$  and the sum curve (from bottom to top:  $0.00873$ ,  $0.0613$ , and  $0.183\text{ mol kg}^{-1}$ ) at  $23\text{ }^\circ\text{C}$ .



**Fig. 4** The relative integrated band intensity,  $A_i$  of the  $\text{H}_3\text{PO}_4$  mode  $\nu\text{P}=\text{O}$  at  $1178\text{ cm}^{-1}$  (filled squares) and the mode of  $\text{H}_2\text{PO}_4^-$ ,  $\nu_s\text{PO}_2$  at  $1077\text{ cm}^{-1}$  (open squares) versus the stoichiometric  $\text{H}_3\text{PO}_4$  concentration at  $23\text{ }^\circ\text{C}$ .

$1160\text{ cm}^{-1}$  which is of very weak band intensity. Nevertheless, band intensity correction for  $\nu\text{P}=\text{O}$  at  $1178\text{ cm}^{-1}$  ( $\text{H}_3\text{PO}_4$ ) has to be taken into account (see experimental section).

In  $\text{D}_3\text{PO}_4(\text{aq})$  solutions, the dissociation product  $\text{D}_2\text{PO}_4^-(\text{D}_2\text{O})$  is detectable by the mode  $\nu_s\text{PO}_2(\text{D}_2\text{O})$  which occurs at  $1084\text{ cm}^{-1}$ . As mentioned, the spectral features of the dissociation product  $\text{H}_2\text{PO}_4^-/\text{D}_2\text{PO}_4^-$  have led to confusion in the older literature (*cf.* ref. 6,14). The vibrational spectra of  $\text{H}_3\text{PO}_4$  and its deuterated analog in fairly dilute phosphoric acid solution are discussed ( $m_T < 1.10\text{ mol kg}^{-1}$ ) because in concentrated solutions,<sup>9-12</sup> the bands shift and broaden considerably and coalesce. The phosphoric acid molecules occur in these concentrated solutions as associated species.<sup>8-12</sup> On the other hand, in very dilute solutions ( $m_T < 0.01\text{ mol kg}^{-1}$ ) the bands of the dissociation product  $\text{H}_2\text{PO}_4^-(\text{aq})$  dominate the spectrum of  $\text{H}_3\text{PO}_4(\text{aq})$ .

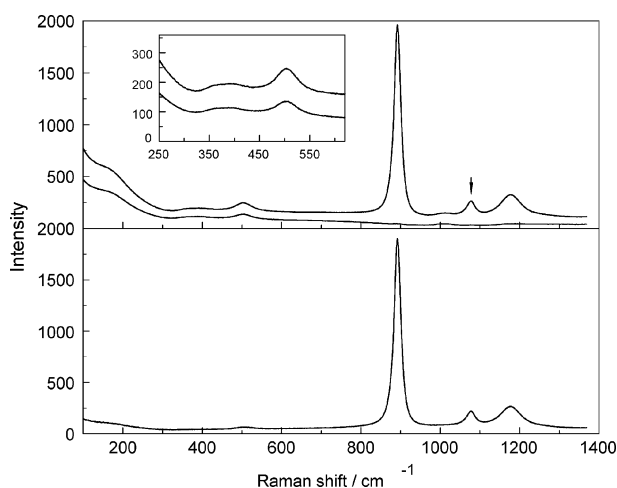
**Table 5** Raman data of the PO<sub>4</sub> modes of H<sub>3</sub>PO<sub>4</sub>(aq) at 23 °C

$\nu_{\max}/\text{cm}^{-1}$	Intensity	fwhh $\text{cm}^{-1}$	Depolarization degree	Assignment
357	1.3	45	0.75	$\rho\text{O}=\text{P}(\text{OH})_3$
394.5	3.4	60	0.75	$\delta_{\text{as}}\text{P}(\text{OH})_3$
499	9.3	54	0.65	$\delta_{\text{s}}\text{P}(\text{OH})_3$
890.1	100	19.5	0.005	$\nu_{\text{s}}\text{P}(\text{OH})_3$
1008	0.9	18	0.75	$\nu_{\text{as}}\text{P}(\text{OH})_3$
1178	22.5	53	0.095	$\nu\text{P}=\text{O}$
1255	2	40	0.12	$\delta\text{PO}-\text{H}$

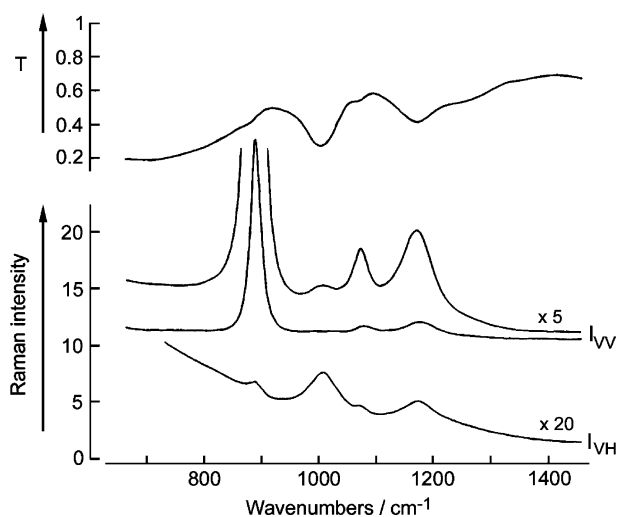
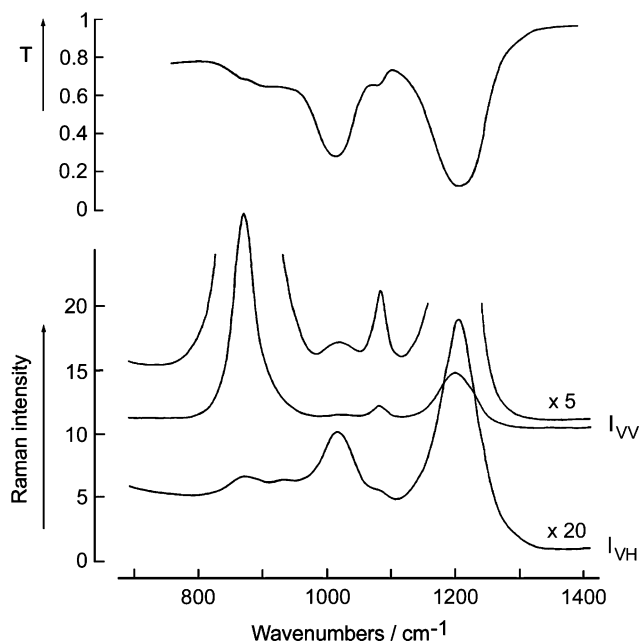
**Table 6** Raman data of the modes in dilute D<sub>3</sub>PO<sub>4</sub> solutions at 23 °C

$\nu_{\max}/\text{cm}^{-1}$	Intensity	fwhh $\text{cm}^{-1}$	Depolarization degree	Assignment
364	1	44	0.75	$\rho\text{O}=\text{P}(\text{OD})_3$
374	3	58	0.75	$\delta_{\text{as}}\text{P}(\text{OD})_3$
494	9.2	52	0.62	$\delta_{\text{s}}\text{P}(\text{OD})_3$
870	100	17.5	0.006	$\nu_{\text{s}}\text{P}(\text{OD})_3$
935	2.5	~34	0.14	$\delta\text{PO}-\text{D}$
1018	0.9	18	0.75	$\nu_{\text{as}}\text{P}(\text{OD})_3$
1194	20	50	0.095	$\nu\text{P}=\text{O}$

With the knowledge of the H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq) influence on the spectrum of H<sub>3</sub>PO<sub>4</sub>(aq) a detailed discussion of the spectrum of phosphoric acid is given. An overview Raman spectrum (100–1400 cm<sup>-1</sup>) of a 0.756 mol kg<sup>-1</sup> (0.728 mol L<sup>-1</sup>) H<sub>3</sub>PO<sub>4</sub> solution is shown in Fig. 5 and the spectroscopic results for H<sub>3</sub>PO<sub>4</sub>(aq) are summarized in Table 5 and for D<sub>3</sub>PO<sub>4</sub>(D<sub>2</sub>O) in Table 6. The Raman and infrared spectra in the P–O stretching region (700–1400 cm<sup>-1</sup>) of a 1.560 mol kg<sup>-1</sup> (1.450 mol L<sup>-1</sup>) H<sub>3</sub>PO<sub>4</sub>(aq) are given in Fig. 6 and for a 1.393 mol kg<sup>-1</sup> (1.430 mol L<sup>-1</sup>) D<sub>3</sub>PO<sub>4</sub>(D<sub>2</sub>O) in Fig. 7.

**Fig. 5** Raman spectrum of a 0.756 mol kg<sup>-1</sup> (0.728 mol L<sup>-1</sup>) H<sub>3</sub>PO<sub>4</sub> at 23 °C. The arrow indicates the mode at 1077 cm<sup>-1</sup> of H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. Upper panel:  $I_{\text{VV}}$  and  $I_{\text{VH}}$  scattering; the inset shows the deformation modes at an expanded scale. Lower panel: isotropic spectrum.

In the overview Raman spectrum of H<sub>3</sub>PO<sub>4</sub>(aq) (Fig. 5) two band regions become visible, the deformation region and the P–O stretching region. The deformation modes in H<sub>3</sub>PO<sub>4</sub>(aq) show an accidental overlap so that only two instead of three modes are to be observed: a depolarized double mode, very poorly resolved with maxima at 357 and 395 and a polarized mode at 499 cm<sup>-1</sup>. The deformation modes are of low intensities (see Table 5 and Fig. 5).

**Fig. 6** Infrared (top) and Raman spectrum ( $I_{\text{VV}}$  and  $I_{\text{VH}}$  scattering) of a 1.560 mol kg<sup>-1</sup> (1.450 mol L<sup>-1</sup>) H<sub>3</sub>PO<sub>4</sub> solution at 23 °C.**Fig. 7** Infrared (top) and Raman spectrum ( $I_{\text{VV}}$  and  $I_{\text{VH}}$  scattering) of a 1.393 mol kg<sup>-1</sup> D<sub>3</sub>PO<sub>4</sub> solution at 23 °C.

In D<sub>3</sub>PO<sub>4</sub>(D<sub>2</sub>O) these modes occur at 364, 374 and 494 cm<sup>-1</sup> (see Table 6).

The P–O stretching mode at 890 cm<sup>-1</sup> is the band with the highest intensity in the Raman spectrum and is also strongly polarized. This mode is assigned to the symmetrical stretching mode of the P(OH)<sub>3</sub> group,  $\nu_{\text{s}}\text{P}(\text{OH})_3$ . The mode at 1008 cm<sup>-1</sup> is of much lower intensity than  $\nu_{\text{s}}\text{P}(\text{OH})_3$ . The mode is depolarized and assigned to the antisymmetric stretch of the P(OH)<sub>3</sub> group,  $\nu_{\text{as}}\text{P}(\text{OH})_3$ . The intensity ratio  $A_{890}/A_{1008}$  for the modes  $\nu_{\text{s}}\text{P}(\text{OH})_3$  and  $\nu_{\text{as}}\text{P}(\text{OH})_3$  is ~ 110 : 1. In the infrared absorption spectrum the intensity ratio  $A_{890}/A_{1008}$  reverses to that in the Raman effect because  $\nu_{\text{s}}\text{P}(\text{OH})_3$  is very weak and  $\nu_{\text{as}}\text{P}(\text{OH})_3$  is of strong intensity (see Fig. 6).

The  $\nu\text{P}=\text{O}$  mode in H<sub>3</sub>PO<sub>4</sub>(aq) should be observed analogous to comparable phosphoryl compounds OPX<sub>3</sub> (X = Cl, Br, OR

**Table 7** Raman band parameters ( $I_{\text{VV}}$  scattering) of a 0.252 mol kg<sup>-1</sup> (0.248 mol L<sup>-1</sup>) H<sub>3</sub>PO<sub>4</sub> as a function of temperature:  $\nu\text{P}=\text{O}$ ,  $\nu_s\text{P}(\text{OH})_3$  and the band of the dissociation product H<sub>2</sub>PO<sub>4</sub><sup>-</sup>

$T/^\circ\text{C}$	H <sub>3</sub> PO <sub>4</sub> ( $\nu\text{P}=\text{O}$ )		H <sub>3</sub> PO <sub>4</sub> ( $\nu_s\text{P}(\text{OH})_3$ )		H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ( $\nu_s\text{PO}_2$ )	
	$\nu_{\text{max}}/\text{cm}^{-1}$	fwhh $\text{cm}^{-1}$	$\nu_{\text{max}}/\text{cm}^{-1}$	fwhh $\text{cm}^{-1}$	$\nu_{\text{max}}/\text{cm}^{-1}$	fwhh $\text{cm}^{-1}$
24.5	1178	53.5	891.2	19.5	1077.6	21.5
32.0	1178	54.0	890.5	19.5	1077.8	22.0
43.0	1182	55.0	888.5	19.3	1078	22.5
57.0	1185.5	58.0	888.0	19.3	1078.5	23.2
69.5	1186	59.5	887.0	19.3	1079	23.5
82.5	1191	62.0	886.5	19.5	1080	24.0
99.7	1193	64.0	885.5	19.8	1081	24.5

with R alkyl and aryl) between 1200–1400 cm<sup>-1</sup> (e.g. ref. 43). The precise peak position depends on the group X inasmuch as X with increasing electronegativity shifts  $\nu\text{P}=\text{O}$  to higher wavenumbers. In liquid trimethyl ester of the phosphoric acid, OP(OCH<sub>3</sub>)<sub>3</sub>,  $\nu\text{P}=\text{O}$  occurs at ~1270 cm<sup>-1</sup>. This value should certainly be expected for phosphoric acid as well. However, in dilute solutions of H<sub>3</sub>PO<sub>4</sub>(aq)  $\nu\text{P}=\text{O}$  occurs at 1178 cm<sup>-1</sup> as a relatively broad band of medium intensity but as a strong band in the infrared. The  $\nu\text{P}=\text{O}$  mode at ~1194 cm<sup>-1</sup> in D<sub>3</sub>PO<sub>4</sub>(D<sub>2</sub>O) is overlapped with the broad deformation mode  $\delta\text{DOD}$  of the solvent D<sub>2</sub>O at 1208 cm<sup>-1</sup>. From the PO–H bands<sup>‡</sup>, mentioned above, the in-plane-deformation mode of the PO–H group,  $\delta\text{PO-H}$  is of very weak intensity and broad in the Raman effect and appears at 1250 cm<sup>-1</sup>. Although broad it is of medium intensity in the infrared spectrum (see Fig. 6). In the spectrum of D<sub>3</sub>PO<sub>4</sub>(D<sub>2</sub>O) the deformation mode shifts to considerably lower wavenumbers due to the isotope shift:

$$\frac{\nu(\text{D})}{\nu(\text{H})} = \sqrt{\frac{2.014}{1.008}} = \sqrt{1.998} = 1.414$$

and appears as a weak broad mode at 935 cm<sup>-1</sup> (Fig. 7). The factor of the isotope effect 1.344 is smaller than the theoretically expected value but in the usual range for such an isotope effect (anharmonicity of the modes). The above mentioned  $\nu_s\text{P}(\text{OH})_3$  mode also shows an isotope effect but much more moderately:  $\sqrt{\frac{\nu_{\text{P(OD)}}}{\nu_{\text{P(OH)}}}} = \sqrt{\frac{18.0135}{17.007}} = \sqrt{1.0592} = 1.029$ . In

D<sub>3</sub>PO<sub>4</sub>(D<sub>2</sub>O)  $\nu_s\text{P}(\text{OD})_3$  occurs at 870 cm<sup>-1</sup> and the observed isotope shift is 1.023, again a little smaller than the theoretical one.

The considerable wavenumber shift of the P=O stretching mode in H<sub>3</sub>PO<sub>4</sub>(aq) compared with  $\nu\text{P}=\text{O}$  for neat OP(OCH<sub>3</sub>)<sub>3</sub> at ~1270 cm<sup>-1</sup> is caused by strong H-bonds of the type P=O...HOH formed in aqueous solutions of phosphoric acid. The P–OH groups are also H-bonded with water molecules of the type P–OH...OH<sub>2</sub> although the H-bond strength is somewhat weaker compared to the ones between P=O and water.<sup>44</sup> As a result of the H-bond formation the protons are somewhat weakened and the stretching mode  $\nu_s\text{P}-(\text{OH})_3$  shows noticeably  $\pi$ -bonding contributions. Therefore, higher stretching peak positions are observed as normally considered with the normal P–O single bonds. Due to the H-bonds formed the PO–H stretching mode

<sup>‡</sup> The  $\gamma\text{PO-H}$  mode, the out of plane deformation, is only observable in the hydrate melt and the most concentrated solution at ~815 cm<sup>-1</sup>, the  $\nu\text{PO-H}$  mode is detectable in concentrated solutions as a broad mode at ~2880 cm<sup>-1</sup> the so called A band. A broad mode at 2350 cm<sup>-1</sup> is assigned to 2 x  $\delta\text{PO-H}$ , the B band and a much weaker one at 1700 cm<sup>-1</sup>, to 2 x  $\gamma\text{PO-H}$  as C band.

( $\nu\text{O-H}$ ) should be down shifted. However, in the dilute solutions studied the broad and weak  $\nu\text{OH}$  mode is completely overlapped with the OH stretching mode of water and shall therefore not be discussed in this context (see footnote 1).

In aprotic, polar organic solvents such as acetonitrile, acetone, tetrahydrofuran and dioxane) in which crystalline H<sub>3</sub>PO<sub>4</sub> is at least sparingly soluble the mode  $\nu\text{P}=\text{O}$  occurs at 1240 cm<sup>-1</sup> in the infrared absorption spectrum.<sup>45</sup> In aprotic solvents the acceptor group P=O cannot form H-bonds unless the solution is fairly concentrated and therefore the wavenumber position for P=O is similar to the one for the trimethylester. (In concentrated H<sub>3</sub>PO<sub>4</sub> solutions auto-association may occur; a formation of H-bonded phosphoric acid molecules).

The DFT data (see Tables 1 and 2) reinforce the interpretation of the presented vibrational data in going from the H<sub>3</sub>PO<sub>4</sub> molecule *in vacuo* to H<sub>3</sub>PO<sub>4</sub>(aq). The mode  $\nu\text{P}=\text{O}$  shifts from 1384.4 cm<sup>-1</sup> down to 1245.8 cm<sup>-1</sup>. Furthermore, the mode  $\nu_s\text{P}(\text{OH})_3$  shifts from 839.4 cm<sup>-1</sup> up to 849.8 cm<sup>-1</sup>. This tendency found by the DFT calculations has been observed by vibrational spectroscopy. Even if the static model applied by the calculations does not reproduce the measured band positions precisely, the trend of the modes depicts the situation of the measured spectral data correctly. The geometric parameters of H<sub>3</sub>PO<sub>4</sub>(vacuo) and H<sub>3</sub>PO<sub>4</sub>(aq) is presented in Table 3. The phosphoryl bond P=O is much shorter than the three single P–O bonds. Furthermore, the P=O bond lengthens slightly in going from H<sub>3</sub>PO<sub>4</sub>(vacuo) to H<sub>3</sub>PO<sub>4</sub>(aq) whilst the P–O bond shortens slightly. At least in dilute solutions the PO<sub>4</sub> unit cannot be considered as a tetrahedral unit as has been done in ref.34

In order to study the hydration in phosphoric acid solution in the Raman effect it would be helpful to study the phosphoric acid in apolar organic solvents such as CCl<sub>4</sub> or to study the temperature effect on the modes of H<sub>3</sub>PO<sub>4</sub>(aq). Unfortunately, phosphoric acid is almost insoluble in this apolar solvent (cf. ref.45) and therefore a temperature dependent Raman study has been applied.

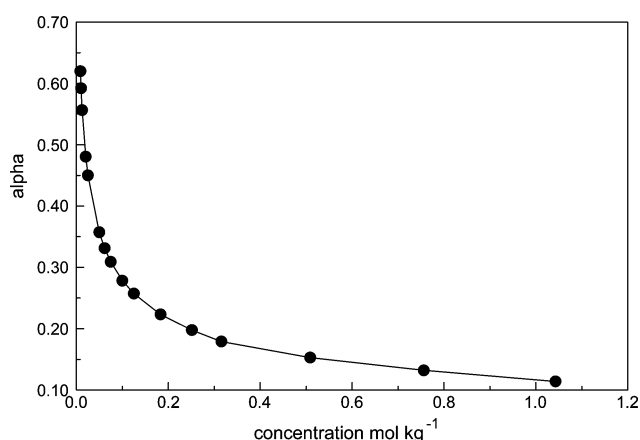
In Table 7 the results of the temperature dependent Raman spectra of a 0.251 mol kg<sup>-1</sup> (0.248 mol L<sup>-1</sup>) phosphoric acid are presented (mol-ratio H<sub>3</sub>PO<sub>4</sub>:H<sub>2</sub>O = 1:224). At 25 °C  $\nu\text{P}=\text{O}$  at 1178 cm<sup>-1</sup> (fwhh = 53 cm<sup>-1</sup>) shifts with temperature to higher wavenumbers and broadens. At 99.7 °C  $\nu\text{P}=\text{O}$  is located at 1193 cm<sup>-1</sup> (fwhh = 64 cm<sup>-1</sup>). The symmetric stretching mode  $\nu_s\text{P}(\text{OH})_3$ , located at 25 °C at 891 cm<sup>-1</sup> shifts slightly to lower wavenumbers and at 99.7 °C this mode is positioned at 886 cm<sup>-1</sup>. The antisymmetric stretching mode of the P(OH)<sub>3</sub> group,  $\nu_{\text{as}}\text{P}(\text{OH})_3$  is much weaker compared with  $\nu_s\text{P}(\text{OH})_3$  (intensity ratio  $\nu_s\text{P}(\text{OH})_3 : \nu_{\text{as}}\text{P}(\text{OH})_3 = 100 : 0.9$ ) and is located at 1008 cm<sup>-1</sup>.

These results show that the P=O group (H-bond acceptor) forms strong H-Bonds with water and the temperature increase weakens the H-bonds between the P=O group and water and as a result a weakening of the H-bond, P=O...HOH follows. Therefore, the temperature increase resulting in a shift of  $\nu_{\text{P=O}}$  to higher wavelength and a shift of  $\nu_{\text{P(OH)}_3}$  to lower wavenumbers may be explained and demonstrates the hydration of the phosphoric acid in aqueous solution.

In this context it may be mentioned that it is necessary to study dilute solutions of phosphoric acid because with higher phosphoric acid concentrations auto-association between  $\text{H}_3\text{PO}_4$  molecules has been observed and a dimeric phosphoric acid,  $\text{H}_6\text{P}_2\text{O}_8$  (cf. ref. 20,21,28) has been proposed. However, as a result of a carefully conducted study in 3 M  $\text{NaClO}_4$  at 25 °C<sup>23</sup> it was shown that at concentrations up to 0.02 m  $\text{H}_3\text{PO}_4$  it was unnecessary to invoke the existence of any species other than the mononuclear phosphate species. In the dilute phosphoric acids no spectroscopic evidence could be detected for the so called dimer,  $\text{H}_6\text{P}_2\text{O}_8$ . At higher  $\text{H}_3\text{PO}_4$  concentrations however, interactions between  $\text{H}_3\text{PO}_4$  molecules are observable but no specific dimeric structure could be detected rather a three dimensional network of H-bonded phosphoric acid molecules.<sup>9-11</sup> The concentration range of the existence of phosphoric acid molecules associated with each other, so called auto-association depends on the water activity and in phosphoric acid solutions with concentrations higher than  $-1 \text{ mol L}^{-1}$  the association effect begins. In the hydrate melt,  $\text{H}_3\text{PO}_4(\text{l})$ , phosphoric acid molecules are strongly hydrogen bonded with each other forming a 3-dimensional network of small clusters<sup>9-11</sup> which may be compared to the situation in crystalline phosphoric acid where the structure reveals strong H-bonds between the phosphoric acid molecules in the monoclinic crystal.<sup>46</sup>

### 3.2. Quantitative Raman measurements of dilute $\text{H}_3\text{PO}_4(\text{aq})$ and $\text{D}_3\text{PO}_4(\text{D}_2\text{O})$

**Data at 23 °C.** It has been demonstrated that the phosphoric acid spectra are overlapped with the modes of its corresponding base, namely  $\text{H}_2\text{PO}_4^-$ (aq). The only undisturbed mode at  $1077 \text{ cm}^{-1}$  of  $\text{H}_2\text{PO}_4^-$ (aq) has been used for quantitative Raman measurements of the dissociation of  $\text{H}_3\text{PO}_4$  in water and the dissociation degree as a function of concentration has been given in Fig. 8.



**Fig. 8** The dissociation degree,  $\alpha$  versus the stoichiometric concentration of  $\text{H}_3\text{PO}_4$  at 23 °C.

Quantifications in  $\text{D}_3\text{PO}_4$  solutions have been carried out using the mode at  $1084 \text{ cm}^{-1}$  of  $\text{D}_2\text{PO}_4^-$ ( $\text{D}_2\text{O}$ ). To that purpose the equilibrium concentrations of  $\text{H}_2\text{PO}_4^-$  and  $\text{D}_2\text{PO}_4^-$  in  $\text{H}_3\text{PO}_4(\text{aq})$  and  $\text{D}_3\text{PO}_4(\text{D}_2\text{O})$  respectively have been determined using the calibration curves expressed in the experimental section.

Quantitative Raman spectroscopy allows one to calculate the first dissociation step of  $\text{H}_3\text{PO}_4(\text{aq})$  and  $\text{D}_3\text{PO}_4(\text{D}_2\text{O})$  according to eqn (1). The equilibrium constant  $K_1$  for this reaction may be defined as:

$$K_1 = \frac{[\text{H}_3\text{O}^+] \cdot [\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \cdot \frac{\gamma_{\text{H}_3\text{O}^+} \cdot \gamma_{\text{H}_2\text{PO}_4^-}}{\gamma_{\text{H}_3\text{PO}_4}} = Q_1 \cdot Q_\gamma \quad (12)$$

with the equilibrium concentrations for the species  $i$  denoted as  $[i]$  and  $\gamma_i$  the activity coefficients of the species. The activity of  $\text{H}_3\text{PO}_4(\text{aq})$  in the dilute solutions is taken as 1 and for  $K_1$  it follows:

$$K_1 = \frac{[\text{H}_3\text{O}^+] \cdot [\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \cdot \gamma_{\pm}^2 \quad (13)$$

or taking the dissociation degree into account:

$$K_1 = \frac{\alpha^2 \cdot m_{\text{T}}}{1 - \alpha} \cdot \gamma_{\pm}^2 \quad (14)$$

The quantitative results for dilute  $\text{H}_3\text{PO}_4$  and  $\text{D}_3\text{PO}_4$  solutions are given in Tables 8 and 9 and  $\text{p}Q_1$  defined as  $-\log_{10} Q_1$  plotted in Fig. 9 as a function of the square root of the ionic strength. This procedure is only meaningful for dilute solutions and therefore only the most dilute solution data have been applied. Extrapolation to zero concentration results in  $\text{p}K_1$  values for  $\text{H}_3\text{PO}_4(\text{aq})$  and  $\text{D}_3\text{PO}_4(\text{D}_2\text{O})$  at 2.14(1) and 2.42(1) respectively at 23 °C. A compilation of selected experimental constants for the

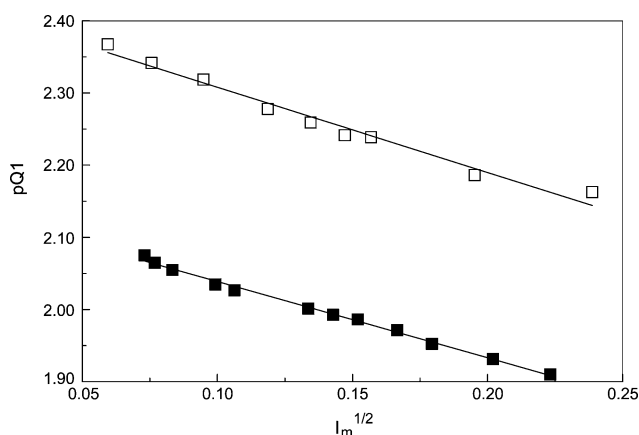
**Table 8** Raman data on the dissociation of  $\text{H}_3\text{PO}_4$  as a function of concentration at 23 °C

$m_{\text{T}} \text{ kg mol}^{-1}$	$[\text{H}_2\text{PO}_4^-]$	$\sqrt{I_{\text{m}}}$	$\alpha$	$\text{p}Q_1$
0.00873	0.00534	0.0733	0.6151	2.0664
0.00994	0.00590	0.0767	0.5926	2.0672
0.0124	0.00695	0.0832	0.5567	2.0609
0.0204	0.00985	0.0987	0.4789	2.0477
0.0249	0.01126	0.1058	0.4502	2.0377
0.0498	0.01785	0.1334	0.3573	2.0046
0.0613	0.0204	0.1425	0.3312	1.9978
0.0748	0.0231	0.1520	0.3088	1.9864
0.0999	0.0278	0.1667	0.2784	1.9697
0.125	0.0322	0.1794	0.2576	1.9517
0.183	0.0408	0.2020	0.2230	1.9314
0.252	0.0498	0.2229	0.1977	1.9121

**Table 9** Raman data on the dissociation of  $\text{D}_3\text{PO}_4$  as a function of concentration at 23 °C

$m_{\text{T}} \text{ kg mol}^{-1}$	$[\text{D}_2\text{PO}_4^-]$	$\sqrt{I_{\text{m}}}$	$\alpha$	$\text{p}Q_1$
0.00644	0.003532	0.0594	0.5485	2.3674
0.0129	0.005719	0.0756	0.4434	2.3415
0.0258	0.00899	0.0948	0.3484	2.3184
0.0516	0.01407	0.1186	0.2727	2.2777
0.0775	0.01809	0.1345	0.2334	2.2590
0.1035	0.02166	0.1472	0.2093	2.2414
0.1295	0.02461	0.1569	0.1900	2.2387
0.2609	0.03810	0.1952	0.1460	2.1861
0.5293	0.05699	0.2387	0.1077	2.1626

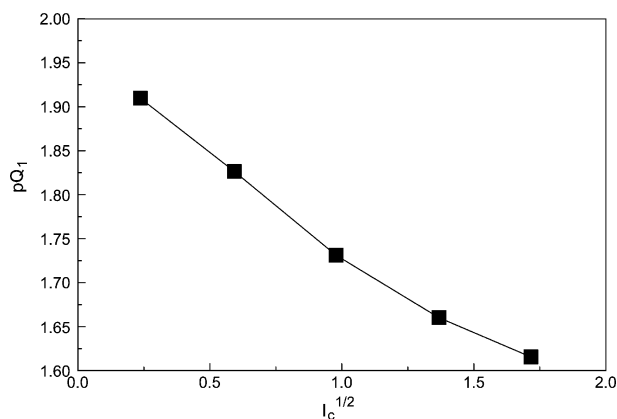




**Fig. 9** The  $pQ_1$  as a function of the square root of ionic strength for  $H_3PO_4(aq)$  (solid black squares) and  $D_3PO_4(D_2O)$  (unfilled squares) at 23 °C.

first dissociation step of phosphoric acid at 25 °C is given in ref. [47] and for heavy phosphoric acid in ref. [48]. The isotope effect on the dissociation of phosphoric acid leads to a higher  $pK_1$  value in heavy phosphoric acid. (The primary and secondary isotope effect is not discernable for phosphoric acid; ultrafast proton exchange.) The  $\Delta pK_1$  value,  $pK_1(H_3PO_4) - pK_1(D_3PO_4)$ , is 0.28(2) in good agreement with a  $\Delta pK_1$  value equal to 0.272<sup>48</sup> determined by potentiometric measurements.

Phosphoric acid solutions with increasing amounts of NaCl become more acid and this fact has been presented for a 0.310 mol L<sup>-1</sup>  $H_3PO_4(aq)$  in Fig. 10. The quantification has been carried out by the second method, namely determining the band ratios of  $A_{1178}/A_{1077}$  (see experimental section). The intensity ratios, the degree of dissociation, the  $pQ_1$  values, the concentration on NaCl and the ionic strength of the phosphoric acid solutions have been given in Table 10. The  $pK_1$  value in a 3 mol L<sup>-1</sup> NaClO<sub>4</sub> solution at 25 °C had been reported by Baldwin and Sillén<sup>23</sup> and the  $pK_1$  value is 1.89 which is much lower than the  $pK_1$  value for zero ionic strength equal to 2.142.<sup>47</sup> The neutral salt effect (NaCl, KCl and tetraethylammonium iodide) on the protonation of phosphate ions in solution as a function of temperature has been studied recently.<sup>32</sup> The neutral salt which competes for water reduces



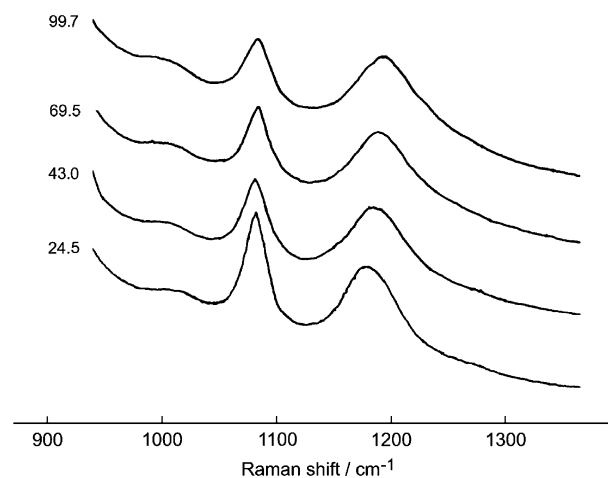
**Fig. 10** The  $pQ_1$  values of a 0.310 mol L<sup>-1</sup>  $H_3PO_4$  solution with increasing amounts of NaCl added (0.0; 0.29; 0.89; 1.80; and 2.87 mol L<sup>-1</sup> NaCl) as a function of the ionic strength,  $I_c$  at 23 °C. Note, the concentration scale is in mol L<sup>-1</sup>.

**Table 10** The influence of NaCl on the degree of dissociation of a 0.310 mol L<sup>-1</sup>  $H_3PO_4$  at 23 °C. Given are the intensity ratios of the bands at 1178 cm<sup>-1</sup> ( $H_3PO_4$ ) and 1077 cm<sup>-1</sup> ( $H_2PO_4^-$ ),  $\alpha$ , the  $pQ_1$  values and the ionic strength

NaCl/mol L <sup>-1</sup>	$A_{1178}/A_{1077}$	$\alpha$	$pQ_1$	$\sqrt{I_c}$
0.00	1.545	0.1804	1.9096	0.2365
0.29	1.390	0.1966	1.8264	0.5924
0.89	1.230	0.2166	1.7312	0.9783
1.80	1.122	0.2326	1.6603	1.3683
2.87	1.058	0.2432	1.61576	1.7162

the hydration of the acid.<sup>49</sup> On a microscopic level, the Na<sup>+</sup>(aq) ion will polarize the phosphoric acid causing the acid strength to increase. Ion pairs with interposed water molecule(s) such as Na<sup>+</sup>(OH<sub>2</sub>)O=P(OH)<sub>3</sub> may be formed. It is interesting to note, that in AlCl<sub>3</sub>- $H_3PO_4$  solutions, direct coordination between Al<sup>3+</sup> and phosphoric acid takes place and species such as Al<sup>3+</sup>...OP(OH)<sub>3</sub> are formed.<sup>12</sup> In the  $H_3PO_4$ -KCl system, on the other hand, no association could be verified.<sup>28</sup> It has been demonstrated that there is essentially no association between orthophosphates and K<sup>+</sup> at 25 °C and Lambert and Watters<sup>51</sup> have reported the value of 10<sup>0.80</sup> for the association quotient for the pyrophosphate complex KP<sub>2</sub>O<sub>7</sub><sup>3-</sup> in 1 M tetramethylammonium bromide at 25 °C but they were unable to detect association of orthophosphate with potassium ions.

**Temperature dependent quantitative Raman measurements on  $H_3PO_4(aq)$ .** Quantitative Raman spectroscopy has been carried out to observe the first dissociation step of a 0.2515 mol kg<sup>-1</sup>  $H_3PO_4(aq)$  in the temperature range from 24.5 °C to 99.7 °C (Fig. 11). The equilibrium constant has been defined according to eqn (14).



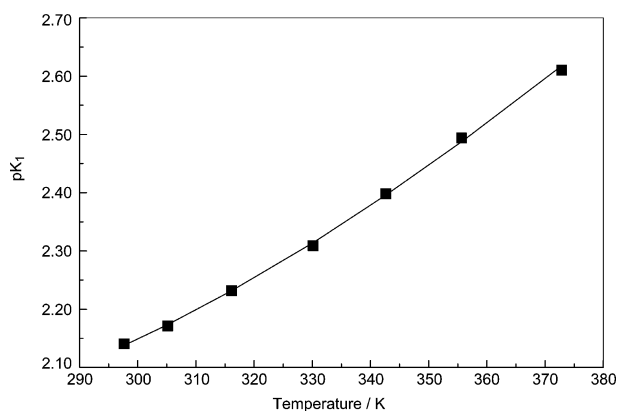
**Fig. 11** Raman spectra of a 0.251 mol kg<sup>-1</sup> (0.248 mol L<sup>-1</sup>)  $H_3PO_4$  solution as a function of temperature (in °C). The most intense band,  $\nu_s P(OH)_3$  at ~890 cm<sup>-1</sup> was omitted for clarity.

In eqn (14) in which the activity coefficient of the undissociated  $H_3PO_4$  has taken unity, and  $\gamma_{\pm}$  is estimated from  $\log \gamma_{\pm} = \frac{A_{\gamma} \cdot \sqrt{I}}{1 + a \cdot B_{\gamma} \cdot \sqrt{I}}$  where  $I_m$  is the ionic strength in molality (m), and the ion size parameter,  $a$  has been taken as 4 Å

**Table 11** Raman data on the dissociation of a 0.251 mol kg<sup>-1</sup> (0.248 mol L<sup>-1</sup>) H<sub>3</sub>PO<sub>4</sub> as a function of temperature

T/K	A* <sub>1178</sub>	A <sub>1077</sub>	[H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ]	α	pQ <sub>1</sub>	pK <sub>1</sub>
297.65	63.05	41.654	0.0468	0.1864	1.9693	2.1407
305.15	62.974	40.073	0.0454	0.1807	1.9995	2.1713
316.15	56.604	33.374	0.0426	0.1695	2.061	2.2316
330.15	55.402	29.6541	0.0392	0.1561	2.1395	2.3091
342.65	52.71	25.242	0.0356	0.1418	2.2303	2.3979
355.65	64.43	27.375	0.0321	0.1276	2.3285	2.4941
372.85	65.4	23.965	0.0281	0.1119	2.4508	2.6141

A\*<sub>1178</sub> means the uncorrected band intensity of νP=O; see text.

**Fig. 12** The temperature dependence of pK<sub>1</sub> of the H<sub>3</sub>PO<sub>4</sub> (temperature range: 297.65–372.85 K); measured data (filled squares) and the fitted curve.

and A<sub>γ</sub> and B<sub>γ</sub> are defined by:  $A_{\gamma} = \frac{1.82482924 \cdot 10^6 \cdot \rho^{1/2}}{(\epsilon T)^{3/2}}$  and  $B_{\gamma} = \frac{50.2915865 \cdot 10^8 \cdot \rho^{1/2}}{(\epsilon T)^{1/2}}$  with ε the static dielectric constant of

water, ρ the density and T in K. The phosphoric acid becomes more molecular as the temperature increases. The measured Raman data at several temperatures for [H<sub>2</sub>PO<sub>4</sub><sup>-</sup>], alpha, the degree of dissociation, logγ<sub>±</sub>, and pK<sub>1</sub> are given in Table 11 and in Fig. 12 the pK<sub>1</sub> values are plotted as a function of temperature. The thermodynamic functions have been obtained by fitting the dissociation constants to an equation of the type:

$$-pK_1 = A/T + B + C \cdot T \quad (15)$$

and the parameters of eqn (15) have been obtained:  $-\log K_1 = 815.36/T - 4.6871 + 0.01373 \cdot T$ . The thermodynamic parameters are defined as follows:

$$\Delta H^0 = 2.3026 \cdot R(A - CT^2) \quad (16)$$

$$\Delta S^0 = 2.3026 \cdot R(B - 2CT^2) \quad (17)$$

and

$$\Delta G^0 = -RT \cdot \ln K_1 = \Delta H^0 - T \cdot \Delta S^0 \quad (18)$$

§ A Raman temperature measurement from 5–301 °C has been carried out and at ~150 °C the phosphoric acid becomes the dominant species. These data will be presented for publication at a later date.<sup>50</sup> In the literature a few high quality data of pK<sub>1</sub> as a function of temperature up to 300 °C have been published<sup>26,31</sup> although the data differ quite considerably at higher temperatures.<sup>31</sup>

with R the gas constant and the parameters A, B, and C given above allow calculation of ΔH<sup>0</sup> according to eqn (16) and with  $-7.76 \text{ kJ mol}^{-1}$ , ΔS<sup>0</sup> equal to  $-67 \text{ J K}^{-1} \text{ mol}^{-1}$  according to eqn (17) and the free enthalpy ΔG<sup>0</sup>  $-12.20 \text{ kJ mol}^{-1}$  according to eqn (18) at 25 °C. These data derived from Raman measurements are comparable to the recommended CODATA given in ref. [47]. Raman spectroscopy is now able to produce high quality data on equilibria HSO<sub>4</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> such as published in<sup>41</sup> and the present data on phosphoric acid. Under normal conditions potentiometric measurements are certainly more suitable than quantitative Raman spectroscopic measurements but under extreme conditions on small sample volumes such as in fluid inclusions or in complex systems the Raman technique certainly has its merits.

## 4. Conclusions

Raman and infrared spectra of dilute solution of H<sub>3</sub>PO<sub>4</sub>(aq) and D<sub>3</sub>PO<sub>4</sub>(D<sub>2</sub>O) have been measured and the bands of the PO<sub>4</sub> skeleton have been assigned to C<sub>3v</sub> symmetry. In addition to the OPO<sub>3</sub> skeleton modes the deformation mode PO–H and PO–D at 1250 and 935 cm<sup>-1</sup> respectively have been obtained. In the Raman and infrared spectra of dilute solutions of H<sub>3</sub>PO<sub>4</sub>(aq) and D<sub>3</sub>PO<sub>4</sub>(D<sub>2</sub>O) no dimeric species of the form H<sub>6</sub>P<sub>2</sub>O<sub>8</sub> and D<sub>6</sub>P<sub>2</sub>O<sub>8</sub> respectively could be detected. Quantitative Raman measurements have been carried out and the first dissociation constant of H<sub>3</sub>PO<sub>4</sub>(aq) and D<sub>3</sub>PO<sub>4</sub>(D<sub>2</sub>O) have been determined at 23 °C. The calculated value of the ΔpK<sub>1</sub>, pK<sub>1</sub>(H<sub>3</sub>PO<sub>4</sub>) – pK<sub>1</sub>(D<sub>3</sub>PO<sub>4</sub>) with 0.28(2) is comparable to the value determined by emf measurements and demonstrates that the heavy phosphoric acid is a weaker acid than its lighter counterpart. The influence of NaCl on the dissociation of H<sub>3</sub>PO<sub>4</sub> has been determined and with increasing amounts of NaCl the phosphoric acid becomes more acidic. Temperature dependent Raman measurements of H<sub>3</sub>PO<sub>4</sub>(aq) have been carried between 24.5 and 99.7 °C. Including the activity coefficients and calculating pK<sub>1</sub> values as a function of temperatures allowed the calculation of the thermodynamic parameters. The acid becomes more molecular with increasing temperature and the stretching band of the P=O group shifts to higher wavenumbers while the symmetric stretch of the P–OH group shifts slightly to lower wavenumbers.

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