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Raman spectroscopic study of a H₂O+Na₂SO₄ solution at 21 to 600 °C and 0.1 MPa to 1.1 GPa: Relative differential ν_1 -SO₄²⁻ Raman scattering cross sections and evidence of the liquid-liquid transition

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Abstract — Relative differential Raman scattering cross sections of the ν_1 -SO₄²⁻ mode in a H₂O+1.54 *m* Na₂SO₄ solution were obtained from in situ experiments at temperatures from 21 to 600 °C and pressures from 0.1 MPa to about 1.1 GPa using a hydrothermal diamond-anvil cell. Additionally, frequency and width of the most intense ν_1 -SO₄²⁻ Raman line were determined for the same solution as a function of temperature and pressure.

The relative differential ν_1 -SO₄²⁻ Raman scattering cross section showed no significant dependence on temperature along the liquid-vapor curve, but a noticeable increase with pressure along the two isochores. In all three cases, however, the changes in the empirically determined relative differential cross section with temperature were smaller than predicted from Bose-Einstein statistics. The implications for quantitative Raman spectroscopy on samples at elevated temperature and pressure are discussed for natural aqueous inclusions and measurements using optical cells.

The determined shifts in the wavenumber ω of the ν_1 -SO₄²⁻ Raman line of unassociated sulfate ions and solvent-separated ion pairs with pressure and temperature can be used to obtain good estimates of the pressure in inclusions or hydrothermal diamond anvil cells. Furthermore, the liquid-liquid transition in the solution was evident from a pronounced decrease in the $(\partial\omega/\partial P)_T$ slope at 200 MPa and an increase in the broadening of the ν_1 -SO₄²⁻ line at the same pressure along

the 21 °C isotherm. In contrast, the transition was reflected with much less certainty in the change of band parameter in the OH stretching region with pressure at the same temperature. Thus, Raman spectroscopy on an appropriate solute species can be used as a sensitive technique to trace the liquid-liquid transition in aqueous solutions in *PTX* space.

1. INTRODUCTION

Working towards quantitative analyses of fluids using Raman spectroscopy was one of the tasks identified already about 25 years ago by Edwin Roedder for the future of inclusion studies: “Improvements in the sensitivity and particularly in the calibration of laser-activated Raman spectroscopy may eventually provide sufficiently accurate determinations of the various S and C species present to permit valid calculations of both pH and Eh, but such calculations require experimental data on speciation at elevated T and P,...” (Roedder, 1984, p. 572).

Today, this task is by no means completed, and there are several obstacles that need to be overcome. One problem is that the relevant species in solution are not always distinguishable from Raman spectroscopy. For example, at least four sulfate species can coexist in significant concentrations in magnesium sulfate solutions, unassociated $\text{SO}_4^{2-}(\text{aq})$ ions and 3 associated species, which include double solvent separated ion pairs $\text{Mg}^{2+}(\text{OH}_2)_2\text{SO}_4^{2-}(\text{aq})$, ion pairs separated by a single water molecule $\text{Mg}^{2+}(\text{OH}_2)\text{SO}_4^{2-}(\text{aq})$, and contact ion pairs $\text{Mg}^{2+}\text{SO}_4^{2-}(\text{aq})$, but only the contact ion pairs can be unambiguously separated from the other 3 sulfate species in Raman spectra of such solutions (Rudolph et al., 2003; Buchner et al., 2004). Thus, Raman spectroscopy may give incomplete information on the speciation, and additional information from application of other techniques must be sought. Moreover, many species in aqueous solutions are rather weak Raman scatterers or can only be studied indirectly via their effect on the Raman spectrum of water, and are often present in relatively small concentrations. Although increasing the laser power lowers the

detection limits, this can result in sample heating and thus change the speciation in the analyzed volume.

Furthermore, it is well known that the Raman efficiency of a species in a fluid scales nonlinearly with density due to increased interaction between the molecules (e.g., Wang and Wright, 1973; Fabre and Oksengorn, 1992; Seitz et al., 1993; Seitz et al., 1996; Knoll et al., 1998). Therefore, relative Raman scattering cross sections of the bands of interest must be known as a function of pressure, temperature, excitation wavelength, and, to some extent, composition to obtain quantitative information from Raman spectra of homogenized fluid inclusions with good accuracy. This is not only of interest in fluid inclusion research. Raman spectroscopy on fluids in hydrothermal diamond-anvil cells is one of the few techniques to study the complexation of light elements in fluids up to the P - T conditions of the lower crust and dehydrating slabs. For example, this technique was utilized to explore contact ion pair formation in an aqueous MgSO_4 solution (Frantz et al., 1994), the change in the silica speciation in H_2O at high pressures and temperatures (Zotov and Keppler, 2002), the complexation of boron in aqueous fluids (Veksler et al., 2002; Schmidt et al., 2005), and the system $\text{H}_2\text{O}+\text{KAlSi}_3\text{O}_8$ to 900 °C and 2.3 GPa (Mibe et al., 2008). For quantification, i.e. to obtain speciation and solubility, Raman band intensities measured in experiments at elevated P and T must be converted into concentrations. This requires information on the change in the relevant Raman cross sections with pressure and temperature, but such data are generally lacking. There are only a few such studies for Raman bands of some non-aqueous fluids (e.g., Wang and Wright, 1973; Fabre and Oksengorn, 1992; Hacura, 1997; Knoll et al., 1998; Gu et al., 2000), and even less is known for Raman active species in aqueous solutions (e.g., Rudolph, 1996; Simonelli and Shultz, 2001).

Therefore, the relative differential Raman scattering cross section of the sulfate stretching mode $\nu_1\text{-SO}_4^{2-}$ in a quartz-saturated $\text{H}_2\text{O}+1.54\text{ m Na}_2\text{SO}_4$ solution was determined in this study as a function of temperature and pressure. These data were obtained at vapor pressure from 22 to 300 °C, along the 1.0587 g/cm^3 isochore from 500 °C, 480 MPa to 200 °C, 8 MPa, and along the 1.1604

g/cm³ isochore from 600°C, 1119 MPa to 100 °C, 122 MPa using a hydrothermal diamond-anvil cell (HDAC). To exclude possible effects of *PVT* anomalies such as the liquid-liquid transition in water (Mirwald, 2005, and references therein), the frequency shift ω and the full width at half maximum $\Gamma_{1/2}$ of the most intense $\nu_1\text{-SO}_4^{2-}$ band component were also determined at these conditions, and additionally along the 21 °C isotherm to a pressure of 837 MPa. A sodium sulfate solution was selected because (1) the sulfate will not be reduced at the conditions of the HDAC experiments of this study, (2) the $\nu_1\text{-SO}_4^{2-}$ mode is strong enough to obtain Raman spectra with a satisfactory signal to noise ratio from solutions in a HDAC, (3) the density along the liquid-vapor curve is known over a relatively wide range of Na₂SO₄ concentrations, and (4) dissolved and precipitated sulfate is common in aqueous fluid inclusions from a variety of geologic environments and the occurrence of sulfate melt inclusions in alkaline rocks was also reported (Roedder, 1984, and references therein; Andreeva et al., 1998; Boiron et al., 1999, Panina, 2005). Analysis of sulfate was thus among the first attempts of quantitative Raman spectroscopy on fluid inclusions (Rosasco and Roedder, 1979; Dubessy et al., 1983) and to obtain direct information on the pH of paleofluids from inclusions, which additionally contained HSO₄⁻ (Dubessy et al., 1992; Boiron et al., 1999).

2. EXPERIMENTAL DETAILS

2.1. Acquisition and processing of the Raman spectra

An externally heated Bassett-type HDAC (Bassett et al., 1993) equipped with near colorless type Ia ultra-low fluorescence and ultra-low birefringence grade diamond anvils (culet diameter 0.9 mm, height 1.9 mm) served as a high P-T optical cell for all experiments. The temperature was measured using two K-type thermocouples attached to the diamonds, and calibrated based on measurements of the ice I-liquid-vapor triple point of water (at 0.01 °C and 0.6 kPa), the ice III-ice I-liquid triple point of water (-21.985 °C, 209.9 MPa), and the α - β quartz transition temperature (574 °C at 0.1

MPa). Accuracy and reproducibility of the temperature measurements were about ± 0.1 to 0.2 °C for temperatures < 25 °C and better than ± 1 °C at temperatures between 100 and 600 °C. The power input to the resistive heaters (Ni-Cr coils around the tungsten carbide seats supporting the anvils) was controlled using Eurotherm® 2408 temperature controllers which held the set temperature within ± 0.2 °C during spectra recording. All heating experiments were conducted at a constant Ar+1% H₂ gas flow to flush the cell interior. This ensured reproducibility of the temperature measurements and prevented oxidation of the HDAC interior.

The sample chamber of the HDAC consisted of a hole (initial diameter 400 μm , initial height 125 μm) in an iridium gasket separating the anvils. At the start, the sample chamber was loaded with a quartz piece, which later served as Raman spectroscopic pressure sensor, and chromatographic grade water (LiChrosolv®, Merck), and sealed by slight compression of the gasket between the anvils. The sample chamber was then cleaned by heating the cell to 600 °C, which converted possible organic contaminants into methane, to avoid fluorescence. After cooling, the sample chamber was opened, the liquid was removed, and a few grains of anhydrous sodium sulfate (Merck), and chromatographic grade water were added. Before the sample chamber was sealed again, an air bubble was allowed to grow by controlled leaking of the liquid until the liquid-vapor volume ratio was about 2. Then, the vapor-saturated mirabilite (Na₂SO₄·10H₂O) dissolution temperature was measured (21.8 ± 0.2 °C). From this temperature, the actual Na₂SO₄ concentration of the solution was determined (1.54 ± 0.02 *m* Na₂SO₄) based on solubility data reported by Linke and Seidell (1965).

During first heating, the bulk density was relatively small, so that monoclinic anhydrous Na₂SO₄ and aqueous sodium sulfate melt formed at temperatures above 300 °C (see supplementary video 18wt%Na2SO4solQz.avi), because H₂O+Na₂SO₄ belongs to the p-q type binary systems. In situ Raman spectra of the liquid phase at a spectrometer position of 1000 cm^{-1} were then recorded along the liquid-vapor curve between 22 and 300 °C. To obtain Raman spectra of the fluid at high temperature and a constant and known Na₂SO₄ concentration, the sample chamber was compressed

further, and the cell was subsequently heated and cooled until the PT path did not intersect the stability field of Na_2SO_4 solid or melt and until isochoric conditions were attained. The latter was indicated if the liquid-vapor homogenization temperature did not change significantly after second heating to the same maximum temperature. In situ Raman spectra of the fluid phase at a spectrometer position of 1000 cm^{-1} were then collected at temperatures to $600\text{ }^\circ\text{C}$ along 2 isochores (1.0587 and 1.1604 g/cm^3). These densities were calculated from the liquid-vapor homogenization temperatures and the data compiled by Potter and Brown (1976). In addition, Raman spectra of quartz were obtained at temperatures from 100 to $500\text{ }^\circ\text{C}$ and at $22\text{ }^\circ\text{C}$ and vapor pressure as reference. The pressure along the 2 isochores was calculated from linear fits of the pressures determined from the calibrated frequency shift of the 464 cm^{-1} Raman line of quartz using the equations (2) and (3) in Schmidt and Ziemann (2000). The determined pressures provide further indication for isochoric behavior, because they display little deviation from the linear fits, and these straight lines do not intersect in the one-phase field (Fig. 1). An additional series of experiments was performed along the $21\text{ }^\circ\text{C}$ isotherm with stepwise increase of the pressure to 837 MPa by compression of the sample chamber. In this case, Raman spectra of the fluid were acquired in the region of the $\nu_1\text{-SO}_4^{2-}$ mode and in the region of the OH stretching vibrations of water, and the pressure was determined by recording Raman spectra of quartz before and after those of the aqueous solution and using the calibrated frequency shift of the 206 cm^{-1} Raman line of quartz and equation (5) in Schmidt and Ziemann (2000). The P - T conditions of the experiments are shown in Fig. 1. The resolution (random error) of the pressure determination was about 10 MPa if the frequency shift of the 206 cm^{-1} Raman line of quartz was used, or about 25 MPa in the case of the 464 cm^{-1} line.

Unpolarized Raman spectra of the solution and of the quartz grain were obtained using a HORIBA Jobin Yvon LabRAM HR800 UV-Vis Raman microprobe (gratings 1800 lines/mm , focal length 800 mm) equipped with a CCD-detector (1024×256 pixel, cooled by a Peltier element). The spectrometer position was 1000 cm^{-1} for the Raman spectra of the fluid in the region of the $\nu_1\text{-SO}_4^{2-}$

mode and the symmetric stretching mode of $\text{H}_4\text{SiO}_4(\text{aq})$, and 450 cm^{-1} for Raman spectra of quartz. In the case of the Raman spectra in the OH stretching region of water, the CCD spectrum covered a wavenumber range between 2700 and 3900 cm^{-1} . The spectra were recorded in backscattering geometry with a Nikon MPlan SLWD 40x objective (numerical aperture 0.4, working distance 14.9 mm) and a confocal pinhole aperture of $100\text{ }\mu\text{m}$. Collection of the backscattered signal was limited by the effective opening angle of the cell of $2\Theta=40^\circ$, corresponding to $\Theta=8.1^\circ$ in the diamond anvil. The 488.0 nm line of an argon ion laser was used for excitation. The laser interference filter was removed to record plasma lines from the Ar^+ laser and Raman lines in the same spectrum. The frequencies of the $\nu_1\text{-SO}_4^{2-}$ band components were calibrated using the plasma lines at 737.28 and 1056.94 cm^{-1} , and those of the band components in the OH-stretching region of water based on the plasma lines at 3167.43 and 3576.86 cm^{-1} . The frequency shift of the quartz lines was calibrated by monitoring the plasma lines at 221.54 , 351.60 , and 529.51 cm^{-1} . The laser power was set to 275 mW at the source. At that laser power, heating of the sample in the HDAC was still insignificant, as determined in a test run from the full widths at half maximum and the frequencies of ruby fluorescence lines as a function of laser power at the source. Use of a higher laser power did not improve the signal to noise ratio due to the increase in the background from fluorescence of the diamonds. No change in the set laser power was noticed during the experiments along the liquid-vapor curve and the two isochores. The laser power was stable within $\pm 3\text{ mW}$ during the measurements along the 21°C isotherm. The collection time for all Raman spectra in the region of the $\nu_1\text{-SO}_4^{2-}$ mode of the solution was 20 accumulations of 20 s each to minimize spectral noise and to achieve low and linear backgrounds of comparable intensity. For spectra in the region of the OH stretching mode, the collection time was 10 accumulations of 10 s each, and for quartz 10 accumulations of 30 s each. Before spectra of the fluid were recorded, the nominal focal point position Δ was always set to the same value to obtain comparable integrated intensities of the Raman bands (Everall, 2000). This was done by focusing on the upper sample chamber surface and then raising the microscope stage by $20\text{ }\mu\text{m}$. The nominal focal point position was measured again

after each spectrum acquisition at $T \geq 100$ °C, because Δ can change by a few μm during spectra recording which is mostly related to the change in the cell height during thermal equilibration with the environment after heating or cooling. During all measurements along the liquid-vapor curve and the two isochores, the HDAC had nearly the same orientation with respect to the polarization of the incident beam.

The spectra were fitted using the software package PeakFit v4.11 from SYSTAT Software Inc., a linear baseline, a symmetric shape (Gaussian-Lorentzian sum (area) model) for the Raman bands of the fluid, and the model Pearson IV for the Raman lines of quartz and the plasma lines to allow for peak asymmetry. Two components were used to fit the spectra in the region of the $\nu_1\text{-SO}_4^{2-}$ mode (Fig. 2), and 3 components for the broad band in the OH-stretching region of water (Brubach et al., 2005). This resulted in an accurate description of the shape of the recorded Raman bands, i.e., nonstatistical residuals were insignificant in all cases. Given the rather poor signal to noise ratio particularly at low intensities, one band component was assumed for the symmetric stretching mode of the silica monomer $\text{H}_4\text{SiO}_4(\text{aq})$, although this band was slightly asymmetric, possibly due to an overlap with additional component at the higher wavenumber side. The analytic areas from the Gauss+Lorentz area fits were used as the integrated intensities A_i of the components.

2.2. Determination of the relative differential $\nu_1\text{-SO}_4^{2-}$ Raman scattering cross section

The intensity I_j of a Stokes Raman signal j from a species i in a fluid in a HDAC can be described by the equation

$$I_j = \left(\frac{\partial \sigma_i}{\partial \Omega} \right)_{\omega_0 - \omega_j, T, P} \frac{x_i}{M_i} N_A V \rho \Omega_{obs} D^{-1} C_\omega F_R F_{Abs} I_0 \quad (1)$$

where ω_0 is the wavenumber of the exciting light, ω_j the Raman shift (i.e., the wavenumber difference of the scattered radiation), $\left(\frac{\partial \sigma_i}{\partial \Omega} \right)_{\omega_0 - \omega_j, T, P}$ the differential Raman scattering cross section of species i at the absolute wavenumber of the Stokes Raman line $\omega_0 - \omega_j$, the temperature T , and the

pressure P , x_i the mole fraction of species i , M_i the molar mass of species i , N_A the Avogadro constant, V the sampled volume, ρ the density of the fluid, Ω_{obs} the limiting solid angle (e.g., defined by the numerical aperture of objective or the effective opening angle of the HDAC), D the area of the detector opening projected on the excitation volume, C_ω a constant to account for the efficiency of the detection system at the wavenumber $\omega_0 - \omega_j$, F_R a factor to account for the intensity decrease due to reflection of incident and exiting light at interfaces between the objective lens and the sample, F_{Abs} a factor to account for the intensity decrease due to absorption of incident and exiting light in the substances between the objective lens and the sample, and I_0 the intensity of the exciting light. Equation (1) is based on an equation given by Schabel (2005), which was modified for the specifics of the experiments reported in this study (unpolarized measurements at different temperatures and fluid densities in backscattering geometry using a HDAC). It is applicable if polarization effects on the Raman line intensity are approximately constant, which is here valid (cell with optically isotropic windows, Raman scattering from a symmetric vibrational mode with a depolarization ratio near zero). Note that Eqn. (1) contains factors such as F_R and F_{Abs} , which are not included in the instrument and component specific Raman quantification factor (Seitz et al., 1987; Pasteris et al., 1988) often used for the determination of concentration ratios in fluid inclusions.

Practically, it is more convenient to use differential Raman scattering cross sections relative to that at a set of reference conditions to obtain concentrations from integrated Raman intensities. This is because absolute Raman scattering cross sections are difficult to determine and measurement conditions (Raman spectroscopic set-up, geometry and optical properties of the fluid inclusion sample or the optical cell) can vary widely. The relative differential $\nu_1\text{-SO}_4^{2-}$ Raman scattering cross sections at elevated P and T reported in this study are based on the reference condition $T=22^\circ\text{C}$ and $P=0.1\text{MPa}$ and were determined from the ratio of integrated $\nu_1\text{-SO}_4^{2-}$ intensities. This requires normalization of the measured integrated $\nu_1\text{-SO}_4^{2-}$ intensities because equation (1) contains

factors other than $\left(\frac{\partial \sigma_i}{\partial \Omega}\right)_{\omega_0 - \omega_j, T, P}$ which cannot be taken as constants for the experiments described

here. These are:

(1) the density of the fluid, because the number of SO_4 -bearing molecules in the sampled volume will increase with density. The density of the fluid was calculated from the determined Na_2SO_4 concentration and the temperature of the experiments at vapor pressure, or from the Na_2SO_4 concentration and the homogenization temperature for the experiments along isochores, based on the data compiled by Potter and Brown (1976).

(2) the intensity decrease due to reflection of incident and exiting light at interfaces. This decrease is large in HDAC experiments in backscattering geometry, because there are 4 media with very different refractive indices (in this study N_2 gas flushing the objective, cover glass, $\text{Ar}+1\%\text{H}_2$ gas, and diamond) between the glass of the objective lens and the fluid in the sample chamber, and thus 10 interfaces, at which reflection occurs. For the derivation of relative Raman scattering cross sections, however, it is only important to know the change in the reflection coefficients at the diamond-fluid interface, which are mainly a function of the P - T dependent index of refraction of the fluid. For all other interfaces, the reflection-related intensity decrease is practically constant. The index of refraction of the fluid n_F was calculated from the density using the Lorentz-Lorenz relationship

$$\frac{(n_F^2 - 1)}{(n_F^2 + 2)\rho} = C \quad (2)$$

where C is a material dependent constant. This is a very good approximation for most materials, as shown, e.g., by Grimsditch et al. (1996) for water to 200 °C and 3.91 GPa. Here, this constant for the sodium sulfate solution was obtained using a refractive index of 1.3595 (Wolf et al., 1981) and a density of 1.1685 g/cm³ (Potter and Brown, 1976) at 22.3 °C, 0.1 MPa. The reflection coefficients R_{in} for the incident light and R_{out} for the exiting light were computed based on the Fresnel equations from the calculated n_F and using a refractive index of diamond of 2.4345 at the wavelength $\lambda=488$

nm for the incident light and 2.4297 at $\lambda=512.5$ nm (the wavelength of $\nu_1\text{-SO}_4^{2-}$) for the exiting light. At all possible angles Θ at which light can be collected (to a maximum of $\approx 15^\circ$ in the fluid), R is only slightly dependent on polarization, with a very near constant average. The factor $F_{R(FD)}$ to account for intensity decrease due to reflection at the fluid-diamond interface was calculated from

$$F_{R(FD)} = (1 - R_{in})(1 - R_{out}) \quad (3)$$

The random error in the density is about ± 0.0025 g/cm³ and the corresponding error in $F_{R(FD)}$ about ± 0.0003 .

The measured integrated $\nu_1\text{-SO}_4^{2-}$ band intensities A_{C1+C2} (sum of the integrated intensities of the band components C1 and C2) were then converted to normalized integrated intensities $A_{C1+C2, \text{norm}}$

$$A_{C1+C2, \text{norm}} = \frac{A_{C1+C2}}{\rho F_{R(FD)}} \quad (4)$$

Finally, the obtained $A_{C1+C2, \text{norm}, PT}$ at the individual PT conditions were then divided by the normalized integrated intensity at the reference temperature $T=22^\circ\text{C}$ and pressure $P=0.1\text{MPa}$. This gives relative differential Raman scattering cross sections of the $\nu_1\text{-SO}_4^{2-}$ mode $\Sigma_{\nu_1\text{-SO}_4^{2-}, PT}$ as a function of P and T at constant excitation wavelength λ_0 (here 488 nm), if polarization effects are insignificant.

$$\Sigma_{\nu_1\text{-SO}_4^{2-}, PT} = \frac{A_{C1+C2, \text{norm}, PT}}{A_{C1+C2, \text{norm}, 0.1\text{MPa}, 22^\circ\text{C}}} = \frac{I_{C1+C2, PT} \rho_{0.1\text{MPa}, 22^\circ\text{C}} F_{R(FD), 0.1\text{MPa}, 22^\circ\text{C}}}{I_{C1+C2, 0.1\text{MPa}, 22^\circ\text{C}} \rho_{PT} F_{R(FD), PT}} = \frac{\left(\frac{\partial \sigma_{\nu_1\text{-SO}_4^{2-}, PT}}{\partial \Omega} \right)}{\left(\frac{\partial \sigma_{\nu_1\text{-SO}_4^{2-}, 0.1\text{MPa}, 22^\circ\text{C}}}{\partial \Omega} \right)} \quad (5)$$

This procedure implies that the sampled volume V can be treated as a constant, but V is a function of the numerical aperture of the objective, the nominal focal point position Δ , and the index of refraction of the fluid n_F (Everall, 2000), and the latter two factors vary slightly in the HDAC experiments described here. However, an increase in the sampled volume is coupled with a flattening of the laser intensity profile (Everall, 2000). For a homogeneous sample, it can thus be expected that the recorded integrated intensity of a Raman band is, to some extent, independent of

V . Figure 3 demonstrates that a small difference in Δ at constant n_F had generally a negligible effect on the integrated intensity of the ν_1 -SO₄²⁻ Raman band measured in this study, with one exception. Thus, no attempt was made to correct A_{C1+C2} for differences in V and the laser intensity distribution in the sampled volume. The data at 200 °C, 8 MPa display a larger deviation (Fig. 3). Because their average is very close to the data at 200 °C, 2 MPa (at the liquid-vapor curve), this deviation reflects the reproducibility of the integrated intensity measurements, rather than a difference in V .

Furthermore, no correction of the measured integrated intensity for the temperature dependence of the absorption in diamond at 488 nm and 512.6 nm (the wavelengths of the laser light and the ν_1 -SO₄²⁻ Raman line) was required. Only type Ib diamonds display a significant increase in the absorption of visible light with temperature (van Enkevort and Versteegen, 1992). Absorption measurements of the type Ia diamond anvil used in this study between 25 and 300 °C using a Bruker IFS 66v spectrometer showed no recognizable temperature dependence in the visible region.

3. RESULTS AND DISCUSSION

3.1. Frequency shift and linewidth of the ν_1 -SO₄²⁻ Raman band as functions of temperature and pressure

The spectra of the silica saturated 1.54 *m* Na₂SO₄ solution recorded at a spectrometer position of 1000 cm⁻¹ displayed a fairly intense Raman band in the region of the ν_1 -SO₄²⁻ mode at 971 to 985 cm⁻¹. Because of the enhanced solubility of quartz with temperature, an additional weak band at about 773 to 780 cm⁻¹ was present at $T \geq 300^\circ\text{C}$, which was assigned to the symmetric stretching mode of H₄SiO₄(aq) (Zotov and Keppler, 2002). The ν_1 -SO₄²⁻ Raman band showed a significant asymmetry at all conditions, and became more asymmetric with temperature (Fig. 2). However, the ν_1 -SO₄²⁻ Raman band shape of ammonium sulfate solutions, which are thought to be fully dissociated, was found to be symmetric up to 200 °C (Rudolph, 1996), and that of sodium sulfate

solutions was symmetric up to 80 °C (Fujita and Kimura, 1981). Consequently, the asymmetry of the $\nu_1\text{-SO}_4^{2-}$ band observed in this study indicates the presence of another sulfate species in the solution. Therefore, this band was deconvoluted into a lower wavenumber component C1 and a higher wavenumber component C2. The much more intense component C2 is assigned to unassociated SO_4^{2-} ions, with Raman indistinguishable contributions from solvent-shared ion pairs $\text{Na}^+(\text{OH}_2)\text{SO}_4^{2-}(\text{aq})$, and doubly solvent-separated ion pairs $\text{Na}^+(\text{OH}_2)_2\text{SO}_4^{2-}(\text{aq})$ (Buchner et al., 1999; Rudolph et al., 2003). The assignment of the $\nu_1\text{-SO}_4^{2-}$ band component C1 is uncertain. Because its integrated intensity displays a positive correlation with the integrated intensity of the $\text{H}_4\text{SiO}_4(\text{aq})$ Raman line (Fig. 4, Tab. 1), it could stem from the sulfate-silicic acid complex $\text{Si}(\text{OH})_4\text{SO}_4^{2-}(\text{aq})$ postulated by Marshall and Chen (1982) from the increase in the solubility of amorphous silica in Na_2SO_4 solutions with temperature above 150 °C. The Raman shifts and full widths at half maximum of the $\nu_1\text{-SO}_4^{2-}$ band reported here are those of component C2, but the relative differential Raman cross sections were calculated from the sum of the integrated intensities of both components to account for the indicated change in sulfate complexation with pressure and temperature.

Figure 5 shows the obtained Raman shifts and full widths at half maximum of the $\nu_1\text{-SO}_4^{2-}$ component C2 at constant Na_2SO_4 molality and silica saturation as a function of pressure along isotherms. At the P - T conditions of this study, the change in the wavenumber with pressure $(\partial\omega/\partial P)_T$ is approximately constant, about $6.5 \text{ cm}^{-1}\text{GPa}^{-1}$, for the isotherms from 100 to 500 °C. The slightly larger $(\partial\omega/\partial P)_T$ along the 100 °C isotherm is probably an overestimate, because it is only based on two data in a small pressure interval. Along the 21 °C isotherm, the change in the frequency with pressure is, within error, initially the same as that of the isotherms at higher temperatures. However, the $(\partial\omega/\partial P)_T$ slope decreased to $4.2 \text{ cm}^{-1}\text{GPa}^{-1}$ at a pressure of about 200 MPa. This slope change is significant because the error in the determined Raman shifts and pressures is about the size of the symbols in Fig. 5 or smaller. Also, it can be ruled out that it is an

artifact from the calibration of the frequency shift of the 206 cm^{-1} Raman line of quartz with pressure by Schmidt and Ziemann (2000), which is a smooth function and is based on measurements using a non-aqueous pressure medium (alcohol). Thus, the pronounced decrease in the $(\partial\omega/\partial P)_T$ slope observed at 200 MPa along the $21\text{ }^\circ\text{C}$ isotherm reflects a response of the S-O bond to a change in the molecular environment of the sulfate ion, likely a transition to a less compressible dynamic structure, and can be attributed to the liquid-liquid transition in water. This interpretation is supported by the results of various experimental studies at similar P - T conditions (e.g., Okhulkov et al., 1994; Cavaille et al., 1996; Mishima and Stanley, 1998; Kawamoto et al., 2004; Mirwald, 2005). The $(\partial\omega/\partial P)_T$ values along the isotherms from 200 to $500\text{ }^\circ\text{C}$ are very similar to the initial slope of the $21\text{ }^\circ\text{C}$ isotherm to 200 MPa (about $6.5\text{ cm}^{-1}\text{GPa}^{-1}$), but the data along the 200 to $500\text{ }^\circ\text{C}$ isotherms extend to higher pressures (Fig. 5). This points to a positive $(\partial P/\partial T)_X$ slope of the liquid-liquid transition in a $1.54\text{ m Na}_2\text{SO}_4$ solution, if the transition still exists at $T \geq 200\text{ }^\circ\text{C}$. Furthermore, the agreement in the $(\partial\omega/\partial P)_T$ values of the isotherms indicates that the obtained relative differential Raman cross sections given in the next section were not affected by PVT anomalies.

The pressure dependence of the line width of the $\nu_1\text{-SO}_4^{2-}$ component C2 displays, likewise, a distinct change in the slope at 200 MPa along the $21\text{ }^\circ\text{C}$ isotherm (Fig. 5). At 500 to $200\text{ }^\circ\text{C}$, Γ decreases slightly with pressure. In contrast, the line width increases along the 21 and $100\text{ }^\circ\text{C}$ isotherms. Because the C2 component consists of contributions of at least two species, the observed anomalous band broadening with pressure at low temperatures (Fig. 5) may be related to different wavenumber shifts $(\partial\omega/\partial P)_T$ of the individual species, possibly coupled with a change in the speciation at the liquid-liquid transition.

The pressure of the liquid-liquid transition in the aqueous $1.54\text{ m Na}_2\text{SO}_4$ solution at $21\text{ }^\circ\text{C}$ observed in this study (about 200 MPa) is in good agreement with literature data from compression experiments on water+salt systems. Cavaille et al. (1996) found anomalous features at $0.2 \pm 0.1\text{ GPa}$ in a Raman spectroscopic study of the behavior of OH stretching mode of water, 2 M KBr , and 2 M

NaCl with pressure at 292 K. Mirwald (2005) reported the occurrence of an inflection in the dehydration curve of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ at 12 °C, 0.27 GPa.

The liquid-liquid transition in the 1.54 *m* Na_2SO_4 solution is also reflected in the pressure dependence of some band parameter in the OH stretching region along the 21 °C isotherm (Fig. 6), but with a much higher uncertainty compared to the results for the $\nu_1\text{-SO}_4^{2-}$ component C2 shown in Fig. 5. Still, changes in the slopes are noticeable at approximately 200 to 400 MPa, particularly for the full widths at half maximum and the contributions to the total peak area of the 3 bands in the OH stretching envelope. However, the intrinsic large error in the band parameter from fits of very broad and largely overlapping band components makes it difficult to reliably interpret their dependence on pressure and obtain reasonably accurate *PTX* data for the liquid-liquid transition in aqueous solutions from Raman spectroscopic studies of the OH stretching region of water. As demonstrated here, determination of Raman band parameter of solute species as a function of *P* and *T* can be much more appropriate for this purpose.

3.2. Temperature and pressure dependence of the relative differential $\nu_1\text{-SO}_4^{2-}$ Raman scattering cross section

Table 1 lists the obtained relative differential Raman scattering cross sections of the $\nu_1\text{-SO}_4^{2-}$ mode $\Sigma_{\nu_1\text{-SO}_4^{2-}, PT}$ for the experiments along the liquid-vapor curve and along isochores of the silica-saturated 1.54 *m* Na_2SO_4 solution, the experimental conditions, $\nu_1\text{-SO}_4^{2-}$ band parameter, calculated corrections, and the integrated intensities of $\text{H}_4\text{SiO}_4(\text{aq})$ Raman band. No attempt was made to calculate $\Sigma_{\nu_1\text{-SO}_4^{2-}, PT}$ from the experiments along the 21 °C isotherm, because no data for the density of the fluid were available. In addition, the sample chamber height was already very small due to stepwise compression of the gasket, and it could not be ensured particularly at the highest pressures that the sampled volume was always located entirely in the liquid. This had no effect on Raman shift and line width of the $\nu_1\text{-SO}_4^{2-}$ mode along the 21 °C isotherm discussed in the previous

section. The $\Sigma_{\nu_1-\text{SO}_4^{2-},PT}$ reported here should not be confused with the relative normalized differential Raman scattering cross sections Σ_j presented by Schrötter and Klöckner (1979). These Σ_j are at constant reference pressure and temperature, for vibrational bands of different gas species normalized to the scattering cross section of N_2 at 2331 cm^{-1} .

The measured integrated $\nu_1\text{-SO}_4^{2-}$ intensity $I_{\text{C1+C2}}$ becomes rapidly smaller with temperature along the liquid-vapor curve (Fig. 7), which is primarily caused by the decrease in the fluid density (Tab. 1). Band broadening (Fig. 3, Tab. 1), and in some cases development of a new band due to contact ion pair formation (Rudolph et al., 2003), additionally contribute to the difficulty to obtain high-temperature Stokes Raman spectra of sulfate solutions with an acceptable signal to noise ratio. Still, the results of this study indicate that Raman spectra of a quality sufficient to determine band parameter with good accuracy can be acquired even at temperatures well above 600°C in HDAC experiments if sulfate concentration and fluid density are high.

The obtained relative differential Raman scattering cross section $\Sigma_{\nu_1-\text{SO}_4^{2-},PT}$ is practically constant along the liquid-vapor curve (Fig. 7). In contrast, there is a noticeable increase with temperature along the two isochores, i.e., $\Sigma_{\nu_1-\text{SO}_4^{2-},PT}$ displays a positive correlation with pressure. Ignoring anharmonic contributions, the temperature dependence of the Stokes scattering cross section due to the population of energy states can be calculated from

$$n + 1 = (1 - e^{-hc\omega_j/k_B T})^{-1} \quad (6)$$

where n is the Bose-Einstein factor, h the Planck constant, c the speed of light, k_B the Boltzmann constant and T the absolute temperature (e.g., Long, 1977; Rudolph and Irmer, 2007). However, the empirically determined $\Sigma_{\nu_1-\text{SO}_4^{2-},PT}$ along the liquid-vapor curve or the isochores show smaller changes with temperature than predicted from Bose-Einstein statistics (Fig. 7). This can be interpreted as an effect of bond expansion with temperature, which counteracts the increase in the scattering cross section related to the population of energy states (Lucazeau, 2003) because the Raman scattering cross section is a function of the derivative of the polarizability with respect to the

mass-weighted normal coordinate of the vibration (e.g., Long, 1977; Rudolph and Irmer, 2007).

Measured Raman intensities are often corrected for their temperature and frequency dependence based on the following or a similar equation (e.g., Brooker et al., 1988)

$$I_j = S_i N_i F_{AS} F_\omega (n+1) I_0 \quad (7)$$

where S_i is the intrinsic molal scattering activity of species i at ω_j , N_i the number of molecules of species i , F_{AS} a collection of apparatus and sample related factors (e.g., detection efficiency, absorption), and F_ω the combined scattering and frequency factor ($F_\omega = (\omega_0 - \omega_j)^3 \omega_j^{-1}$ in the case of photon counting). Note that F_ω has only a small effect (<1.2%) on the relative integrated ν_1 -SO₄²⁻ intensities at the conditions of this study and its non-consideration does therefore not explain the difference between the calculated and the observed behavior of the ν_1 -SO₄²⁻ Raman scattering cross section with temperature. The important consequence of this difference for quantitative Raman spectroscopy is that, in addition to an appropriate calibration, the actual changes in the Raman scattering cross section with temperature and pressure must be known for the determination of the concentration of a species from the integrated intensity of one Raman band at elevated P - T conditions. In such experiments, approximation of the temperature dependence of the Raman scattering cross section based on the Bose-Einstein factor (Zotov and Keppler, 2002) can result in a substantial error in the obtained concentration, particularly at high temperatures and low pressures.

The $\Sigma_{\nu_1\text{-SO}_4^{2-}, PT}$ reported in this study can be used to quantify the concentration of sulfate species in a sample at elevated temperature and pressure (e.g., after dissolution of a sulfate daughter mineral in a fluid inclusion) based on the ratio of the integrated ν_1 -SO₄²⁻ intensities obtained from the Raman spectrum at elevated P and T and that at the reference pressure and temperature in the same focus position, and applying the appropriate normalizations (see section 2.2, particularly Eqn. 1). A good estimate of the pressure in the inclusion or in the optical cell can be obtained from the Raman shift of the ν_1 -SO₄²⁻ component ω_{C2} determined in this study as a function of P and T . This should be done relative to the ν_1 -SO₄²⁻ Raman shift at a reference P - T condition to minimize

compositional effects. Furthermore, the sulfate concentration must be known at the reference pressure and temperature. For hydrothermal diamond-anvil cells experiments, the concentration at the reference condition can serve as internal standard in the case of relatively simple systems. This is because it can be determined from solubility data, e.g., via measurement of the vapor-saturated liquidus temperature if that temperature is lower than the reference temperature, or, with a lower accuracy, from the full width at half maximum of the ν_1 -SO₄²⁻ Raman line at 23 °C, 0.1 MPa (e.g., Rudolph et al., 2003). In an analogous manner, the approach described here can also be used to study solubility and fluid speciation in other systems using diamond-anvil or other optical cells. The prerequisites are that the species concentrations at the reference condition are known and high enough for acquisition of the relevant Raman lines with sufficient signal to noise ratio, that the density and other variables required for normalization can be approximated reasonably well, and that relative differential Raman scattering cross sections are available.

Compared to optical cells, for which all important measurement conditions are usually known well, Raman spectroscopic concentration determinations in fluid and melt inclusions are considerably more difficult using the approach described in the previous paragraph. This is mainly because an external standard (synthetic fluid inclusions, preferentially in the same host mineral, or standard solutions) is required in most cases. The factors Ω_{obs} , V , ρ , F_R , and F_{Abs} (see Eqn. 1) need to be either equal or known for external standard and sample, but can be very different and problematic to quantify (particularly F_R and V). In addition, the measured intensity of a Raman line from an inclusion can depend on the orientation of the sample due to polarization in optically anisotropic hosts. Interference with Raman lines from the host mineral and fluorescence can also impair the analyses. These and other specifics of quantitative Raman spectroscopy on natural fluid inclusions were discussed in detail e.g., by Rosasco and Roedder (1979) and Pasteris et al. (1988).

For the measurements on standard and sample at the reference conditions, the uncertainties can be minimized if integrated intensities ratios of the Raman lines of the species to be analyzed and of another species are determined, a practical method that is widely applied in fluid inclusions studies

(e.g., Rosasco and Roedder, 1979; Seitz et al., 1987, Dubessy et al., 1992). For example, Rosasco and Roedder (1979), Dubessy et al. (1983), Boiron et al. (1999) used the ratio of the integrated ν_1 - SO_4^{2-} or ν_s - $\text{SO}_3(\text{HSO}_4^-)$ intensity to that of the deformation band at 1640 cm^{-1} or the OH stretching region of water to calibrate the concentrations of sulfate and hydrogen sulfate in aqueous solutions. It would be desirable to also use the water bands as an internal standard for heated aqueous inclusions. However, the integrated intensities of the Raman bands of water vary with temperature, pressure, and composition (e.g., Walrafen, 1962; Frantz et al., 1993; Dubessy et al., 1999; Guillaume et al., 2003), and, as shown here, the Raman scattering cross section of the species of interest is also a function of temperature and pressure. Therefore, the assumption that the ratio of the Raman scattering cross sections at high P and T equals that at the reference condition may not hold. The same applies to the F_{Abs} ratio because absorption in the inclusion host can strongly depend on the wavelength and temperature. Therefore, utilization of the integrated intensity of water Raman bands as an internal reference at elevated temperature and pressure demands a rather extensive calibration in addition to the knowledge of the inclusion depth and light absorption behavior of the host.

Such calibrations are not required if it can be ensured that the position of the laser focus in the inclusion is practically the same during the analyses at the reference and at the elevated temperature. In such favorable cases, the species concentration at elevated temperature can be obtained from the known species concentrations at the reference condition multiplied with the ratio of the normalized integrated ν_1 - SO_4^{2-} intensities at elevated and reference temperature. The integrated ν_1 - SO_4^{2-} intensities should be normalized for the changes in the Raman scattering cross section, e.g., using the $\Sigma_{\nu_1-\text{SO}_4^{2-}, PT}$ determined in this study, in the density and, if significant, in F_R and F_{Abs} . For sulfate melt inclusions, the $\Sigma_{\nu_1-\text{SO}_4^{2-}, PT}$ reported here should be applied with caution because of the different chemical environment. In practice, suitable inclusions would be relatively thick and their nearest surface to the surface of the polished section would be fairly plane and approximately parallel. In addition, the thickness of the host mineral above the inclusion should be

as small as possible to minimize the effect of inclusion depth on F_{Abs} , Ω , laser intensity profile, and vertical extent of the focus (Rosasco and Roedder, 1979; Everall, 2000), i.e. accuracy and precision of the measurements will decrease with inclusion depth.

The situation is more advantageous if concentration ratios can be determined from integrated intensities of Raman bands from comparable vibrational modes at similar frequencies (e.g., $\nu_1\text{-SO}_4^{2-}$ at about 980 cm^{-1} and $\nu_s\text{-SO}_3(\text{HSO}_4^-)$ at about 1050 cm^{-1}). In such cases, possible differences in the absorption of the Raman light in the host will be insignificant or small, and the assumption is reasonable that the ratio of the Raman scattering cross sections can be taken as independent of temperature, pressure, and composition. This is supported by the study by Rudolph (1996), who found that the isotropic molal scattering coefficients $S(\nu_1\text{-SO}_4^{2-})$ and $S(\nu_s\text{-SO}_3(\text{HSO}_4^-))$ relative to that of $\nu_1\text{-ClO}_4^-$ did not change significantly from 22 to 200 °C and 25 to 280 °C in different aqueous solutions at vapor pressure, resulting in a near constant ratio $R=1.32166=\sigma(\nu_1\text{-SO}_4^{2-})/\sigma(\nu_s\text{-SO}_3(\text{HSO}_4^-))$. Consequently, the $\text{HSO}_4^-/\text{SO}_4^{2-}$ concentration ratio in heated fluid inclusion can be determined in a simple way and with an accuracy similar to that of Raman spectroscopic analyses at room temperature. This is important for the study of hydrothermal paleofluids because the $\text{HSO}_4^-/\text{SO}_4^{2-}$ equilibrium, which can be used to obtain information on the pH, is strongly temperature dependent. Therefore, the $\text{HSO}_4^-/\text{SO}_4^{2-}$ ratio should be measured in a fluid inclusion heated to its formation temperature to obtain a representative value. There are still very few studies in which it was attempted to estimate the pH of inclusion fluids based on Raman spectroscopic analyses of species concentration ratios. Dubessy et al. (1992) and Boiron et al. (1999) determined the $\text{HSO}_4^-/\text{SO}_4^{2-}$ ratio in fluid inclusions at room temperature and found evidence for very acidic fluids in retrograde metamorphic quartz veins (pH of 1 ± 1). Measurements at elevated temperature can potentially improve such estimates. However, exact determination of the pH in a natural fluid at high temperature is mainly impeded by insufficient knowledge of the activity coefficients and the equilibrium constant.

4. SUMMARY AND CONCLUDING REMARKS

The Raman shift, the full width at half maximum, and changes in the integrated intensity of the $\nu_1\text{-SO}_4^{2-}$ mode of a silica-saturated 1.54 *m* Na_2SO_4 solution were determined as a function of temperature along the liquid-vapor curve and along two isochores to 600 °C and 1.1 GPa. Application of a hydrothermal diamond-anvil cell has allowed these measurements over a larger range in pressures than accessible by conventional optical cells. This approach has yielded new data on the effects of pressure and temperature on the Raman scattering cross section of the $\nu_1\text{-SO}_4^{2-}$ mode, which showed significant deviations from the temperature dependence predicted from Bose-Einstein statistics. Consequently, quantitative Raman spectroscopy on samples at high *P* and *T* to study speciation and solubility requires knowledge of the actual changes of the relevant Raman scattering cross sections, with the probable exception of concentration ratio determinations of similar species based on Raman bands from comparable molecular vibrations.

The obtained relative differential Raman scattering cross sections $\Sigma_{\nu_1\text{-SO}_4^{2-}, PT}$ can be applied to the determination of sulfate concentrations in inclusions or optical cells at elevated temperature and pressure. If required for such measurements, good estimates of the pressure can be obtained from the shift in the wavenumber of the $\nu_1\text{-SO}_4^{2-}$ Raman line based on the results reported here for unassociated sulfate ions and solvent-separated ion pairs. More generally, a method is described to empirically obtain the temperature and pressure dependence of Raman scattering cross sections for other geologically relevant species in aqueous solutions (e.g., H_4SiO_4^0 , CO_3^{2-} , HCO_3^- , borate ions) to be used for solubility and speciation studies on such Raman active species up to the conditions of the lower crust and dehydrating slabs. In addition, specific aspects of quantitative Raman spectroscopy on fluid inclusions at elevated temperature are discussed.

Furthermore, the results of this study suggest that sulfate-silicate complexation can be substantial in aqueous solutions at high temperatures. The ν_1 -SO₄²⁻ Raman band of the silica-saturated Na₂SO₄ solution showed a second component, the fraction of which increased with temperature, and which occurred at a lower wavenumber than the more intense component assigned to unassociated SO₄²⁻ ions and solvent-separated ion pairs. The positive correlation of integrated intensity of this lower-wavenumber sulfate component with the integrated intensity of the H₄SiO₄(aq) Raman line points to a sulfate-silicic acid complex, perhaps Si(OH)₄SO₄²⁻(aq) as postulated by Marshall and Chen (1982).

Lastly, the results presented above on the frequency and linewidth of the ν_1 -SO₄²⁻ mode of the 1.54 *m* Na₂SO₄ solution at 21 °C reveal a distinct decrease in the $(\partial\omega/\partial P)_T$ slope from 6.5 to 4.2 cm⁻¹GPa⁻¹ at 200 MPa and an increased broadening of the ν_1 -SO₄²⁻ line at the same pressure. This anomalous behavior is interpreted as a response of the S-O bond to a change in the molecular environment of the sulfate ion due to the liquid-liquid transition in the solvent. The evidence from the change of band parameter in the OH stretching region of water with pressure at the same temperature was much less conclusive. Therefore, accurate measurements of frequency and linewidth of an appropriate Raman band of a solute species can be used to trace the liquid-liquid transition in aqueous solutions in *P-T-X* space to study the conditions at which this transition can affect their properties and be relevant for geologic fluids.

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Figure captions

Figure 1. Pressure-temperature conditions of the experiments. Open diamonds = experiments along liquid-vapor curve; filled square = experiment at a fluid density of 1.0447 g/cm^3 ; open squares = experiments along the 1.0587 g/cm^3 isochore; open circles = experiments along the 1.1604 g/cm^3 isochore; filled circles = experiments along 21°C isotherm; filled diamonds = phase transitions at lower bulk density (cp., supplementary video), pressures estimated from phase diagrams (Ravich and Borovaya, 1964), a = nucleation of monoclinic Na_2SO_4 , b = dissolution of vapor, c = melting of Na_2SO_4 crystal, d = dissolution of Na_2SO_4 melt; solid lines = isochores; dashed line = portion of liquid-vapor curve; dotted lines = non-isochoric runs.

Figure 2. In situ Raman spectra of the silica-saturated 1.54 m Na_2SO_4 solution in the region of the sulfate symmetric stretching mode $\nu_1\text{-SO}_4^{2-}$, a) at 300°C , 521 MPa , showing the fitted baseline, the two components, and the sum (grey line) curves, b) at several temperatures along the 1.1604 g/cm^3 isochore from 600°C , 1120 MPa to 100°C , 120 MPa . Intensities are shown as recorded, no correction was applied. The decrease in the background with temperature is mostly related to the decrease in the diamond fluorescence.

Figure 3. Sum of the integrated intensities of both $\nu_1\text{-SO}_4^{2-}$ band components A_{C1+C2} vs. Δ , the nominal distance of the focal point to the fluid/upper anvil interface. n_F = index of refraction of the fluid.

Figure 4. Integrated intensity A_{C1} of $\nu_1\text{-SO}_4^{2-}$ band component C1 vs. integrated intensity $A_{\text{H}_4\text{SiO}_4}$ of the $\text{H}_4\text{SiO}_4(\text{aq})$ Raman line at about 775 cm^{-1} .

Figure 5. Raman shift and full width at half maximum of the $\nu_1\text{-SO}_4^{2-}$ Raman band component C2

of the 1.54 *m* Na₂SO₄ solution as a function of pressure along isotherms. Number in parentheses = $(\partial\omega/\partial P)_T$ slope in cm⁻¹GPa⁻¹.

Figure 6. Parameter of the 3 deconvoluted bands (P1 – circles, P2- squares, P3 – diamonds) in the region of the OH stretching mode of water as a function of pressure at 21 °C.

Figure 7. Measured integrated ν_1 -SO₄²⁻ intensity A_{C1+C2} (sum of band components C1 and C2), normalized to A_{C1+C2} at 22 °C, 0.1 MPa, and relative differential Raman scattering cross section of the ν_1 -SO₄²⁻ mode $\Sigma_{\nu_1-\text{SO}_4^{2-}, PT}$ of the 1.54 *m* Na₂SO₄ solution as a function of temperature.

Diamonds = data for liquid-vapor curve, circles = data for 1.0587 g/cm³ isochore, squares = data for 1.1604 g/cm³ isochore. Thick grey line = temperature dependence of the Stokes ν_1 -SO₄²⁻ Raman scattering cross section predicted from Bose-Einstein factor using Eqn. (6) and the measured Raman shifts ω_{C2} (grey crosses).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Table 1. Conditions and results of the experiments along the liquid-vapor curve and along isochores of the quartz-saturated $\text{H}_2\text{O}+1.54 \text{ m Na}_2\text{SO}_4$ solution, and calculated relative differential $\nu_1\text{-SO}_4^{2-}$ Raman scattering cross sections.

T (°C)	P (MPa)	Δ (μm)	Th(L+V→L) (°C)	ρ (g/cm^3)	n_F	$F_{R(\text{FD})}$	ω_{C2} (cm^{-1})	$\Gamma_{1/2,C2}$ (cm^{-1})	A_{C2}	$\omega_{C1}^{\S}$ (cm^{-1})	$\Gamma_{1/2,C1}^{\S}$ (cm^{-1})	A_{C1}	A_{C1+C2}	$\Sigma_{\nu_1\text{-SO}_4^{2-}}$, PT	$A_{\text{H}_4\text{SiO}_4}$
22.3	0.1	20	P _v	1.1685	1.3595	0.8463	981.10	7.0	15897 (574)	975.0	17.6	761 (671)	16657	1.000	b.d.l.
100	0.1*	20	P _v	1.1275	1.3455	0.8413	979.02	7.1	15364 (321)	972.9	15.4	684 (388)	16048	1.004	b.d.l.
200	2*	23	P _v	1.0506	1.3197	0.8318	976.57	9.1	14106 (143)	966.8	16.5	591 (177)	14697	0.998	b.d.l.
200	2*	20	P _v	1.0506	1.3197	0.8318	976.49	9.1	14178 (114)	967.4	12.9	497 (129)	14676	0.997	b.d.l.
300	9*	26	P _v	0.9247	1.2782	0.8159	974.16	11.7	12266 (96)	961.4	14.8	362 (95)	12627	0.994	169 (99)
300	9*	21	P _v	0.9247	1.2782	0.8159	974.20	11.7	12214 (103)	962.3	15.2	483 (109)	12697	0.999	75 (49)
550	530	18	206	1.0447	1.3177	0.8311	971.17	15.9	14070 (324)	960.3	21.3	2032 (368)	16102	1.101	1153 (63)
500	480	20	191.5	1.0587	1.3224	0.8328	972.22	15.2	14741 (146)	959.1	17.8	1183 (154)	15925	1.072	833 (75)
450	402	17	191.5	1.0587	1.3224	0.8328	973.10	14.0	14297 (303)	963.0	20.4	1735 (349)	16032	1.080	502 (72)
450	402	20	191.5	1.0587	1.3224	0.8328	973.09	14.1	14506 (234)	962.2	20.0	1529 (271)	16036	1.080	521 (76)
400	323	20	191.5	1.0587	1.3224	0.8328	973.87	13.0	14420 (336)	964.6	19.5	1606 (386)	16026	1.079	487 (97)
300	165	20	191.5	1.0587	1.3224	0.8328	975.31	11.1	14439 (178)	965.1	17.1	1029 (211)	15468	1.042	413 (74)
200	8	16	191.5	1.0587	1.3224	0.8328	976.72	9.0	14463 (230)	968.8	16.2	739 (277)	15202	1.024	b.d.l.
200	8	20	191.5	1.0587	1.3224	0.8328	976.73	9.0	13736 (335)	969.7	16.9	721 (394)	14458	0.974	b.d.l.
600	1119	23	39 [#]	1.1604	1.3567	0.8454	973.44	17.3	16090 (209)	959.8	22.1	1672 (237)	17762	1.075	2304 (76)
600	1119	18	39 [#]	1.1604	1.3567	0.8454	973.54	17.0	15775 (256)	960.6	22.8	2111 (295)	17886	1.082	2215 (68)
500	920	18	39 [#]	1.1604	1.3567	0.8454	974.97	15.0	16277 (282)	964.1	21.1	1950 (325)	18226	1.103	923 (103)
400	720	20	39 [#]	1.1604	1.3567	0.8454	976.39	12.9	16409 (306)	966.9	19.2	1573 (354)	17982	1.088	549 (132)
300	521	20	39 [#]	1.1604	1.3567	0.8454	977.63	11.0	16039 (125)	967.2	14.7	962 (137)	17001	1.029	517 (77)
200	321	20	39 [#]	1.1604	1.3567	0.8454	978.77	8.9	15778 (311)	971.8	15.4	1073 (363)	16851	1.020	b.d.l.
100	122	20	39 [#]	1.1604	1.3567	0.8454	979.94	7.1	15641 (452)	975.1	13.7	811 (512)	16452	0.996	b.d.l.
100	122	17	39 [#]	1.1604	1.3567	0.8454	979.93	7.3	15856 (144)	972.2	13.9	555 (178)	16410	0.993	b.d.l.

T = temperature; P = pressure; Δ = nominal distance of focal point and fluid/upper anvil interface, average of measurements before and after spectrum acquisition, $\pm 2 \mu\text{m}$; Th(L+V→L) = liquid-vapor homogenization temperature, homogenization to the liquid phase; ρ = density; n_F = calculated refractive index of the fluid; $F_{R(\text{FD})}$ = factor to account for intensity decrease due to reflection at the fluid/diamond interface; ω_{C2} and ω_{C1} = Raman shift of $\nu_1\text{-SO}_4^{2-}$ band components C2 and C1; $\Gamma_{1/2,C2}$ and $\Gamma_{1/2,C1}$ = full width at half maximum of band components C2 and C1; A_{C2} and A_{C1} = integrated intensity of band component C2 or C1 (20 s accumulation time), number in parentheses = standard error; A_{C1+C2} = integrated intensity of the $\nu_1\text{-SO}_4^{2-}$ mode, sum of band components C1 and C2; $\Sigma_{\nu_1\text{-SO}_4^{2-},\text{PT}}$ = relative differential Raman cross section of the $\nu_1\text{-SO}_4^{2-}$ mode; $A_{\text{H}_4\text{SiO}_4}$ = integrated intensity of the $\text{H}_4\text{SiO}_4(\text{aq})$ band at about 775 cm^{-1} , C1 (20 s accumulation time), number in parentheses = standard error; P_v = experiment at vapor pressure, * = pressure estimated from phase diagrams (Ravich and Borovaya, 1964); [#] = from intersection of isochore with liquid-vapor curve, vapor did not nucleate upon cooling; b.d.l. = below detection limit. [§] = Note: the numbers for ω_{C1} and $\Gamma_{1/2,C1}$ should be used with caution, particularly at T<300 °C. Their average standard errors are 80 and 32 times higher than those in ω_{C2} and $\Gamma_{1/2,C2}$ due to the low intensity of C1 and its strong overlap with C2.