A Raman spectroscopic investigation of speciation in La$_2$(SO$_4$)$_3$(aq)†

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Raman spectroscopic measurements have been made of aqueous solutions of La(ClO$_4$)$_3$, La$_2$(SO$_4$)$_3$, and Na$_2$SO$_4$ in water and heavy water, in the terahertz frequency region (40–1400 cm$^{-1}$) and down to low concentrations (0.000263 mol L$^{-1}$). Temperature dependent measurements of a 0.0098 mol L$^{-1}$ La$_2$(SO$_4$)$_3$ solution have been carried out from 23–98 °C. In solutions of La(ClO$_4$)$_3$ with water and heavy water, the [La(OH$_2$)$_9$]$_3^+$ and [La(OD$_2$)$_9$]$_3^+$ have been characterized and a weak, strongly polarized band observed at 343 cm$^{-1}$ and 326 cm$^{-1}$ respectively assigned to the $v_1$ LaO$_9$ mode, the breathing mode of the clusters. In La$_2$(SO$_4$)$_3$(aq), in addition to the $v_1$SO$_4^{2–}$ mode at 980 cm$^{-1}$, a pronounced band component at 991 cm$^{-1}$ has been assigned to an inner-sphere complex (ISC) and a similar $v_1$SO$_4^{2–}$ band contour has been observed in La$_2$(SO$_4$)$_3$ solutions in D$_2$O. Sulfate may act as a monodentate ligand. Conformation of this assignment is provided by the component at 312 cm$^{-1}$ of the [La(OH$_2$)$_9$OSO$_3$]$^+$ species in addition to the band at 343 cm$^{-1}$ for the fully hydrated cluster, [La(OH$_2$)$_9$]$_3^+$. After subtraction of the component of the ISC at 991 cm$^{-1}$, the $v_1$SO$_4^{2–}$ band in La$_2$(SO$_4$)$_3$(aq) showed systematic differences from that in Na$_2$SO$_4$(aq). This is consistent with a $v_1$SO$_4^{2–}$ band at 983.3 cm$^{-1}$ that can be assigned to the existence of an outer-sphere complex (OSCs). The observed change of the degree of sulfato-complex formation with dilution reflects the stepwise sulfato-complex formation. A $K_T$ value has been determined at 0.9 of the equilibrium between OSC and ISC. Temperature dependent measurements on a dilute La$_2$(SO$_4$)$_3$ solution have been taken from 23 °C to 100 °C. The study on the aqueous La$_2$(SO$_4$)$_3$ system. The following aqueous systems have been measured: La(ClO$_4$)$_3$, La$_2$(SO$_4$)$_3$ and Na$_2$SO$_4$. Speciation of these systems has been determined: $\Delta H^\circ = 18.6 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = 62.1 \text{ J mol}^{-1} \text{K}^{-1}$.

1. Introduction

Lanthanum sulfate enneahydrate, La$_2$(SO$_4$)$_3$$\cdot$9H$_2$O, is the most common hydrate of lanthanum sulfate, La$_2$(SO$_4$)$_3$$\cdot$nH$_2$O (n = 1–9)$^3$ and is the only stable hydrate in contact with its solution between 0° and 100°. La$_2$(SO$_4$)$_3$ is sparingly soluble at room temperature and the solubility diminishes with temperature. Lanthanum exists in aqueous solution exclusively in the trivalent state and the La$^{3+}$ ion is strongly hydrated due to its high charge to radius ratio. The coordination number (CN) in the primary hydration shell for La$^{3+}$ in aqueous solution has been determined at nine (data in Table 1, ref. 4). The water molecules of the nonahydrate results in a hydration structure of a tricapped trigonal prism (TPP) with $D_3$ symmetry.$^3$ The O-atoms of the three waters in the equatorial plane (capping position) are separated from the cation by a bond distance of 2.64 Å, while six water molecules at the vertices of the trigonal prism have a La-O bond distance of 2.515 Å.$^{5,6}$ A recent Raman spectroscopic investigation revealed that in concentrated La(ClO$_4$)$_3$(aq) ion pairs are formed while in dilute solutions the undisturbed [La(H$_2$O)$_9$]$_3^+$ species exist.

This study has been undertaken to characterize the species formed in aqueous La$^{3+}$–sulfate solutions over a very broad concentration range and at elevated temperatures. Sulfato-complex formation has been characterized in solutions on a variety of divalent and trivalent metal sulfates$^{7-22}$ and the question arises whether these complexes also occur with La$^{3+}$(aq). The investigation of La$_2$(SO$_4$)$_3$ solutions proved to be especially challenging because lanthanum sulfate is only sparingly soluble in water and the salt shows a retrograde solubility with temperature increase. The study on the aqueous La$_2$(SO$_4$)$_3$ is the first Raman experimental investigation one this dilute system. The following aqueous systems have been measured using Raman spectroscopy at 23 °C: La(ClO$_4$)$_3$, La$_2$(SO$_4$)$_3$ and Na$_2$SO$_4$. Specifically, we have been interested in the vibrational characterization of the La$^{3+}$–aqua stretching band at low...
concentration and the possible formation of ion pairs/complexes between La$^{3+}$ and sulfate. Dilute Na$_2$SO$_4$ solutions have been measured to characterize the sulfate modes free of sulfato-complex species. A La$_2$(SO$_4$)$_3$ solution at 0.0098 mol L$^{-1}$ has been measured from 23 °C to 98 °C in order to characterize the sulfato-complex formation as a function of temperature. Thermodynamic parameters such as enthalpy and entropy of the sulfato-complex formation have been determined from the measured $K_3$ values as a function of temperature.

2. Experimental details

2.1. Preparation of solutions

Lanthanum perchlorate solutions were prepared from La$_2$O$_3$ (Sigma-Aldrich, 99.9%) and HClO$_4$ in a beaker until all oxide dissolved. The lanthanum ion content was analysed by complexometric titration. The solution density was determined with a pycnometer at 23 °C and the molar ratios water per salt were calculated ($R_w$-values). A La(ClO$_4$)$_2$ stock solution was prepared at 2.488 mol L$^{-1}$ ($R_w = 81.54$), 0.498 mol L$^{-1}$ ($R_w = 103.43$) and 0.249 mol L$^{-1}$ ($R_w = 213.75$). The solutions were analysed for dissolved chloride with a 5% AgNO$_3$ solution. The absence of a white AgCl precipitate showed no Tyndall effect and were detected with a cooled CCD detector.

In order to obtain spectra defined as $I(\bar{v})$ which are independent of the excitation wavenumber $\nu_1$, the measured Stokes intensity should be corrected for the scattering factor ($\nu_1 - \langle \bar{v} \rangle$)$^3$. When counting methods are used, the measured count rates have to be corrected with the factor $(\nu_1 - \langle \bar{v} \rangle)^3$.

The depolarization ratio, $\rho$, of the modes were determined according to eqn (4):

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

In the low wavenumber region the $I(\bar{v})$ and $R_Q(\bar{v})$ spectra are significantly different and only the spectra in R-format are presented. It should be noted that one of the advantages of using isotropic $R$-spectra is that the baseline is almost free of ionic contributions.

2.2. Spectroscopic measurements

Raman spectra were measured in the macro chamber of the T 64000 Raman spectrometer from Jobin Yvon in a 90° scattering geometry at 23 °C. These measurements have been described elsewhere in detail. Briefly, the spectra were excited with the 514.5 nm line of an Ar$^+$ laser at a power level of 1100 mW at the sample. After passing the spectrometer in subtractive mode, with gratings of 1800 grooves per mm, the scattered light was detected with a cooled CCD detector. $I_{VV}$ and $I_{VH}$ spectra were obtained with fixed polarisation of the laser beam by rotating the polariser at 90° between the sample and the entrance slit to give the scattering geometries:

$$I_{VV} = I(\bar{v}[ZZX]) = 45\alpha^2 + 4\gamma^2$$

$$I_{VH} = I(\bar{v}[ZYX]) = 3\gamma^2.$$
intensities, $I_R$, with $I_R = (A_{980}/A_{991})C_{NH3ICO}$ were calculated. The quantity $I_R$ is directly proportional to the concentration of the species of interest and thus: $I_R = JC$. From the slope of the curve, $I_R = JC$, the so called relative molar scattering coefficient, $J$, was obtained. For $r_1$ SO$_4^{2-}$ at 980 cm$^{-1}$, it follows $J_{980} = 0.788$ and for bound sulfate at 991 cm$^{-1}$: $J_{991} = 0.760$.

The equilibrium concentrations of [SO$_4^{2-}$]$_{free}$ and [SO$_4^{2-}$]$_{bound}$ were obtained from the ratios of the areas of “free” SO$_4^{2-}$ mode at 980 cm$^{-1}$ (this mode includes contributions from the fully hydrated sulfate, in the outer-outer-sphere and outer-sphere$^{20-31}$) and the bound SO$_4^{2-}$ mode at 991 cm$^{-1}$ and the relative molar scattering factors. The sum of the equilibrium concentrations [SO$_4^{2-}$]$_{free}$ plus [SO$_4^{2-}$]$_{bound}$ is equal to $C_0$, the stoichiometric concentration of MnSO$_4$ (in mol kg$^{-1}$). The integrated band intensities are $A_{980} = J_{980}[SO_4^{2-}]_{free}$ and $A_{991} = J_{991}[SO_4^{2-}]_{bound} = J_{991}(C_0 - [SO_4^{2-}]_{free})$, where $J_{980}$ and $J_{991}$ are the relative molar scattering factors for the bands at ~980 and 991 cm$^{-1}$. For the ratio of the integrated intensities, $A_{980}/A_{991}$ was calculated as follows:

$$\frac{A_{991}}{A_{980}} = \frac{J_{991}(C_0 - [SO_4^{2-}]_{free})}{J_{980}[SO_4^{2-}]_{free}}$$

and after rearranging for [SO$_4^{2-}$]$_{free}$ it follows:

$$[SO_4^{2-}]_{free} = \frac{C_0}{J_{980} A_{991}} A_{980} + 1$$

With the equilibrium concentration of [SO$_4^{2-}$]$_{free}$ determined and $C_0$, the stoichiometric concentration of La$_2$(SO$_4$)$_3$, known, the degree of bound sulfate, $\alpha$, may be calculated by eqn (8):

$$\alpha = (C_0 - [SO_4^{2-}]_{free})/C_0.$$  

3. Results and discussion

3.1. The unassociated [La(OH$_2$)$_3$]$^{3+}$(aq)

The La$^{3+}$(aq) ion is strongly hydrated in aqueous solution due to its high charge to radius ratio. A recent DFT study on a [Ln(H$_2$O)$_9$]$^{3+}$ cluster imbedded in a polarizable dielectric continuum, taking into account the bulk water resulted in a tricapped trigonal prism (TTP) polyhedron of symmetry $D_3$. The oxygen atoms of three water molecules in the equatorial plane are separated from La$^{3+}$ by a bond distance of 2.64 Å, while six water molecules at the vertices of the trigonal prism are found at an average La–O bond distance at 2.515 Å. The hydration sphere of La$^{3+}$(aq) is labile and a water-exchange rate constant $k_{ex}$ at 25 °C was given at $\approx 2 \times 10^8$ s$^{-1}$. Because of the labile coordination sphere for La$^{3+}$ there is the possibility of a counterion (anion) coordination replacing water from the coordination polyhedron. Although perchlorate is considered a non-complex forming anion, in La(ClO$_4$)$_3$ solutions at high salt concentrations (1.5 mol L$^{-1}$), it was shown that perchlorate forms outer sphere-ion pairs, [La(OH$_2$)$_3$]$^{3+}$-ClO$_4^-$ and at yet higher concentrations perchlorate penetrates into the first hydration sphere of the La$^{3+}$. In La(ClO$_4$)$_3$(aq) at 2.488 mol L$^{-1}$ the mole ratio solute to water is 15.7 and this amount of water is barely enough to completely hydrate the La$^{3+}$ ion while the remaining 6.7 water molecules hydrate the three ClO$_4^-$ ions. In such a concentrated solution contact ion pair formation is simply forced on La$^{3+}$. Therefore, it is necessary to measure dilute La(ClO$_4$)$_3$ solutions but this measurement is hampered by the fact that the La–O breathing mode is very weak and its Raman scattering coefficient, 0.030, is low.

A vibrational analysis of the LaO$_9$ skeleton modes of the [La(OH$_2$)$_3$]$^{3+}$ species ($D_{3h}$ symmetry) has been carried out recently. Twenty four normal modes (n.m.’s) are expected for the LaO$_9$ skeleton modes of the nonahydrate [La(OH$_2$)$_3$]$^{3+}$. The irredicible representation of the vibrational modes is as follows: $I_{ vib}(D_{3h}) = 3a_1(Ra) + 2a_2 + 5e(Ra, i.r.) + 3a_1^2 + 3a_1^2e(i.r.) + 3e^2(Ra)$. Two stretching modes and a bending mode are expected with character $a_1$ and these modes are Raman active only. Two stretching modes and three bending modes occur with character $e'$ and these modes are infrared and Raman active. A stretching mode and two bending modes for character $a_2$ are expected and these n.m.’s are infrared active only while three modes (one stretch and two bending modes) with character $e''$ are only Raman active. The modes with character $a_2'$ and $a_1''$ are torsional modes and are not active. However, it was evident that only the symmetric La–O stretching mode appears in the Raman effect. The remaining LaO$_9$ modes are too weak to be identified in Raman and this has also been observed for other metal ion–oxygen modes in aqueous solution. The La(ClO$_4$)$_3$ solution spectra reveal a Raman mode for the [La(OH$_2$)$_3$]$^{3+}$ species, which is very weak, strongly polarized and broad at 343 cm$^{-1}$. A 0.249 mol L$^{-1}$ La(ClO$_4$)$_3$ solution is presented in Fig. 1. In neither NaClO$_4$(aq) nor HClO$_4$(aq) was this mode observed and must therefore stem from a symmetrical vibration connected to a La–O stretching band.

The perchlorate modes are well characterized so only a brief description is given. The ClO$_4^-$ ion possesses $T_d$ symmetry and has nine modes of internal vibrations spanning the representation $\Gamma_{vb}(T_d) = a_1(Ra) + e(Ra) + 2f_2(Ra, i.r.)$. All n.m. are Raman active, but in i.r. only the $f_2$ modes are active. The spectra of La(ClO$_4$)$_3$(aq) show the predicted four Raman-active bands for the tetrahedral ClO$_4^-$ (aq). The $r_1(a_1)$ ClO$_4^-$ band centred at 931.5 cm$^{-1}$ is totally polarized ($\rho = 0.005$) whereas $r_2(f_2)$ ClO$_4^-$ centred at 1105 cm$^{-1}$ is depolarized as are the deformation modes $r_2(f_2)$ ClO$_4^-$ at 631 cm$^{-1}$ and $r_2(e)$ ClO$_4^-$ at 463 cm$^{-1}$ (Fig. 1).

In addition to the isotropic mode, $r_1$ LaO$_3$ at 343 cm$^{-1}$ (fwhm = 49 ± 2 cm$^{-1}$) a very weak, broad mode centered at 170 ± 10 cm$^{-1}$ can be observed in aqueous La(ClO$_4$)$_3$ solution (isotropic Raman scattering). The mode can also be seen in pure water at ~175 cm$^{-1}$ and is moderately intense but slightly polarized. This mode has been assigned to a restricted translational mode of the H-bonded water molecules and is strongly anion and

$^\dagger$ The datum for $k_{ex}$ at 25 °C was given incorrectly in ref. 4 page 298.
3.2. The unassociated \( \text{SO}_4^{2-} \) (aq)

Unassociated \( \text{SO}_4^{2-} \) (aq), in \( \text{(NH}_4\text{)}_2\text{SO}_4 \) (aq) for instance, has been described in detail.\(^{24}\) Although in \( \text{Na}_2\text{SO}_4 \) solutions at higher concentrations, ion pairs such as outer-outer sphere and outer-sphere ion-pairs are formed, in dilute solutions <0.1 mol \( \text{L}^{-1} \) the equilibrium concentrations are small relative to “free” sulfate. In a 0.101 mol \( \text{L}^{-1} \) \( \text{Na}_2\text{SO}_4 \) solution ~13% of the total sulfate exists as ion pairs, mainly as outer-sphere ion pairs while 87% are considered “free” or unassociated, \( \text{SO}_4^{2-} \) (aq).\(^{25}\) With further dilution, the fraction of ion pairs diminishes significantly and reaches zero at infinite dilution. Therefore, dilute \( \text{Na}_2\text{SO}_4 \) solutions shall be briefly discussed and compared with \( \text{La}_2(\text{SO}_4)_3 \) solutions. An overview Raman spectrum of a 0.101 mol \( \text{L}^{-1} \) \( \text{Na}_2\text{SO}_4 \) (aq) from 100–1900 cm\(^{-1}\) is presented in Fig. 2. The spectral characteristics of the non-associated \( \text{SO}_4^{2-} \) (aq) ion have been conducted.\(^{26}\) Here, however, a brief discussion of the results relevant to the ligated sulfate is presented.

![Fig. 1: Raman scattering profiles of a 0.249 mol \( \text{L}^{-1} \) \( \text{LaClO}_4 \) (aq). Upper panel: \( R_{\text{pol}} \) and \( R_{\text{depol}} \) scattering. Note the very weak band at 343 cm\(^{-1}\) due to the symmetric breathing mode of \( \text{La(OH}_3\text{)}_2 \). In addition, the deformation modes of \( \text{ClO}_4^- \) (aq) which dominate the spectrum at 460 cm\(^{-1}\) and 628 cm\(^{-1}\) are shown. The band at 178 cm\(^{-1}\) \( (R_{\text{vd}}) \) is due to the restricted O–H⋯O bonds of the water H-bond network. Lower panel: Isotropic scattering in R-format. Note the very weak band at 343 cm\(^{-1}\) due to the symmetric breathing L–O mode. The isotropic mode at 182 cm\(^{-1}\) is due to the restricted O–H⋯O bonds of the water H-bond network.](Image 1)

![Fig. 2: Overview Raman profiles of a 0.101 mol \( \text{L}^{-1} \) \( \text{Na}_2\text{SO}_4 \) solution. The \( I_{\text{pa}} \) and \( I_{\text{ps}} \) scattering orientations (upper panel) are given and in the lower panel the isotropic scattering.](Image 3)

The non-associated \( \text{SO}_4^{2-} \) (aq) ion possesses \( T_d \) symmetry and thus nine modes of internal vibration, having the representation: \( I_{\text{vib}}(T_d) = a_1(R) + e(R) + 2f_2(R, IR) \). All vibrational modes are Raman active, one mode with character \( a_1 \) is totally polarized, and three modes with character \( e \) and \( f_2 \) are depolarized but only the \( f_2 \) modes are IR allowed.

In the IR spectrum only two sulfate bands are active, namely \( v_1(f_2) \) and \( v_3(f_2) \) located at 618 cm\(^{-1}\) and 1104 cm\(^{-1}\) respectively\(^{24}\) but all four modes are Raman active. Detailed Raman spectroscopic characterizations of the \( \text{SO}_4^{2-} \) (aq) bands are given in ref. 24. The \( v_1(a_1) \cdot \text{SO}_4^{2-} \) mode is the strongest band in the sulfate spectrum. The band for a 0.101 mol \( \text{L}^{-1} \) \( \text{Na}_2\text{SO}_4 \) (aq) centred on 980.69 cm\(^{-1}\) \( (\text{fwhh} = 6.05 \pm 0.5 \text{ cm}^{-1}) \) is almost totally polarized \( (\rho = 0.0035) \) whereas the \( v_1(f_2) \cdot \text{SO}_4^{2-} \) band centred on 1109 cm\(^{-1}\) \( (\text{fwhh} = 65.0 \text{ cm}^{-1}) \) is depolarized. The deformation modes \( v_3(f_2) \cdot \text{SO}_4^{2-} \) at 614 cm\(^{-1}\) \( (\text{fwhh} = 31 \text{ cm}^{-1}) \) and \( v_2(e) \cdot \text{SO}_4^{2-} \) at 448 cm\(^{-1}\) \( (\text{fwhh} = 35 \text{ cm}^{-1}) \) are depolarized as well.

At low frequencies, a broad and weak mode at 180 cm\(^{-1}\) \( (\text{fwhh} = 168 \text{ cm}^{-1}) \) was observed in the isotropic R-spectrum.\(^{24}\) This mode is also observable in pure water at 175 cm\(^{-1}\) and has been attributed to H-bonded water molecules.\(^{26,27}\) In \( \text{Na}_2\text{SO}_4 \) (aq) it may be assigned to the restricted translational modes of both \( \text{OH}⋯\text{O} \) and \( \text{OH}⋯(\text{OSO}_3)^2^- \) hydrogen-bonds thereby the contribution of the \( \text{OH}⋯(\text{OSO}_3)^2^- \) hydrogen-bonds increases with increasing \( \text{Na}_2\text{SO}_4 \) concentration. In a concentrated, saturated \( \text{Na}_2\text{SO}_4 \) solution, 1.617 mol \( \text{L}^{-1} \), the restricted translational mode, \( v \) \( \text{OH}⋯\text{O} \) was observed at 185 cm\(^{-1}\) with a fwhh at 130 cm\(^{-1}\) while in dilute solutions the restricted translational mode is determined by the \( \text{OH}⋯\text{O} \) hydrogen bonds in water and only slightly influenced by \( \text{OH}⋯(\text{OSO}_3)^2^- \) hydrogen-bonds. The corresponding bending mode of this unit appears at ~60 cm\(^{-1}\).\(^{26,27}\)

The \( v_1 \cdot \text{SO}_4^{2-} \) band shape in dilute \( \text{Na}_2\text{SO}_4 \) (aq) is symmetrical in both Raman polarization arrangements but other band parameters vary slightly with concentration (Fig. 3, panel A and B, data with open squares). For example, at 23 °C for a 1.617
3.3. Raman spectra of La$_2$(SO$_4$)$_3$(aq)

The Raman spectra of La$_2$(SO$_4$)$_3$ in aqueous solution show additional features to those in the unassociated sulfate spectra and the [La(OH$_2$)$_3$]$^{3+}$(aq) mode which have been described above. La$_2$(SO$_4$)$_3$ is only sparingly soluble in water and the Raman signals are therefore of low intensity and the spectra are dominated by the solvent, water. Nevertheless these additional spectroscopic features could be observed and are now discussed in detail.

An overview Raman spectrum of the 0.0376 mol L$^{-1}$ La$_2$(SO$_4$)$_3$ solution is presented in Fig. 4. Because of the low solute concentration, the sulfate bands appear weak and the scattering spectrum is dominated by the bands of the solute, water. The $v_1$(a$_1$) SO$_4^{2-}$ stretching profile shows two band components at 981 cm$^{-1}$ and at 991 cm$^{-1}$. The weak antisymmetric stretching mode, $v_3$ SO$_4^{2-}$ at 1112 cm$^{-1}$ appears broader compared to a comparable Na$_2$SO$_4$ solution. Furthermore, in the terahertz frequency range, the La-O breathing mode, normally at 343 cm$^{-1}$, appears in the difference spectrum of the 0.0376 mol L$^{-1}$ La$_2$(SO$_4$)$_3$ solution as a broad feature at ~328 cm$^{-1}$ with two separate component bands, one at 343 cm$^{-1}$ assigned to the La-O breathing mode of [La(OH$_2$)$_3$]$^{3+}$(aq) and one at 312 cm$^{-1}$ assigned to hydrated La$^{3+}$ where sulfate occurs in the first hydration shell, [La(OH$_2$)$_3$SO$_4$]$^{2+}$(aq) (Fig. 5). With further dilution of La$_2$(SO$_4$)$_3$ the very small scattering coefficient of this La-O breathing mode prevents further observation of this band.

The split of the $v_1$(a$_1$) SO$_4^{2-}$ stretching band into a band at 981 cm$^{-1}$ and a pronounced shoulder at 991 cm$^{-1}$ becomes immediately obvious in Fig. 6B. In Na$_2$SO$_4$(aq) the strongly polarized mode at 991 cm$^{-1}$ is absent while in a variety of divalent and trivalent metal sulfate solutions sulfato-complex species could be observed.$^4,11,12,24$ In Fig. 7, a concentration plot of $v_1$(a$_1$) SO$_4^{2-}$ band profiles are given, showing the concentration dependence of four representative Raman

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**Fig. 3** Concentration effects at 23 °C on the $v_1$-SO$_4^{2-}$ mode at ca. 980 cm$^{-1}$ in Na$_2$SO$_4$ solutions (open circles) and in La$_2$(SO$_4$)$_3$ solutions (after subtraction of the 991 cm$^{-1}$ component, filled circles): (A and C): peak position ($r_{\text{max}}$): (B and D): fwhh.

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mol L$^{-1}$ Na$_2$SO$_4$ solution ($R_w$ = 32.75), $r_{\text{max}}$ for this isotropic band appears at 981.04 cm$^{-1}$ with a fwhh = 6.60 cm$^{-1}$, for a 0.101 mol L$^{-1}$ solution ($R_w$ = 552.2) $r_{\text{max}}$ appears at 980.69 cm$^{-1}$ with a fwhh = 6.05 cm$^{-1}$. For an infinitely dilute solution (extrapolation to zero concentration) the $v_1$-SO$_4^{2-}$ band appears at 980.45 cm$^{-1}$ and a fwhh = (5.55 ± 0.05) cm$^{-1}$. For present purposes, it is relevant that the symmetric profile of the $v_1$-SO$_4^{2-}$ mode is independent of the salt concentration over the entire range studied ($\approx 1.617$ mol L$^{-1}$). The $v_1$-SO$_4^{2-}$ band is the strongest band in the SO$_4^{2-}$(aq) - Raman spectrum and the intensity ratio of $v_1$-SO$_4^{2-}$ band area to $v_3$-SO$_4^{2-}$ band area is 9:1.

The band contour of the antisymmetric S-O stretching mode, $v_3$ SO$_4^{2-}$ is also symmetrical in both polarization arrangements but band parameters vary slightly with concentration. For example, at 23 °C for a 1.617 mol L$^{-1}$ Na$_2$SO$_4$ solution, $r_{\text{max}}$ is found at (1112 ± 2) cm$^{-1}$ and shifted to slightly lower wavenumbers as the concentration was decreased, reaching (1106 ± 2) cm$^{-1}$ at infinite dilution. The fwhh decreased from (76 ± 2) cm$^{-1}$ for a 1.617 mol L$^{-1}$ salt solution to (67 ± 2) cm$^{-1}$ for a 0.100 mol L$^{-1}$ solution reaching (64 ± 2) cm$^{-1}$ at infinite dilution. It is important to state that the symmetric profile of the $v_3$-SO$_4^{2-}$ band which is completely depolarized is independent of the Na$_2$SO$_4$ concentration over the entire range studied (Fig. 2).

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**Fig. 4** Raman scattering profiles (polarized and depolarized) of a 0.0376 mol L$^{-1}$ La$_2$(SO$_4$)$_3$ solution in the low wavenumber region from 200–1900 cm$^{-1}$. In addition to the sulfate modes at 448, 614, 981 and 1112 cm$^{-1}$ the spectrum is dominated by the solvent with its two very broad librational bands at ~455 and ~720 cm$^{-1}$ of water and the deformation mode at 1637 cm$^{-1}$ (I$_{lib}$ scattering). Note that the $v_1$ SO$_4^{2-}$ stretching band, the strongest sulfate band is split into two component bands at 982 and 991 cm$^{-1}$. Both SO$_4^{2-}$ deformation modes at 451 and 614 cm$^{-1}$ appear on the broad librational band profile as weak bands. The $v_3$ SO$_4^{2-}$ antisymmetric stretching band at 1112 cm$^{-1}$ is also of weak intensity.
spectra from 0.0303-0.000263 mol L$^{-1}$. With dilution, the equilibrium concentration of the band at 991 cm$^{-1}$ diminishes while the one of the “free” sulfate rises. The band parameters for the 980 cm$^{-1}$ band and the band at 991 cm$^{-1}$ is given in Table S1.† It is interesting to note that both sulfate stretching modes are strongly polarized and in the anisotropic scattering both component bands appear at 981 and 991 cm$^{-1}$ (Fig. 6B) and the polarization degrees are 0.004 and 0.006 respectively. This spectroscopic observation contradicts the observation made in a similar system, MgSO$_4$(aq), for which a dynamic exchange model was proposed to explain the occurrence of the band at 995 cm$^{-1}$. (The 995 cm$^{-1}$ band in MgSO$_4$(aq), however, is the band of a sulfato-complex species.$^{24,28}$) The deformation bands of sulfate, $v_2$ SO$_4^{2-}$ at 448 cm$^{-1}$ and the band $v_4$ at 614 cm$^{-1}$ are broadened compared to the ones in Na$_2$SO$_4$(aq) of comparable sulfate concentrations [Fig. 2, 3 and 6A]. These two deformation bands are depolarized in the Raman scattering as shown in Fig. 2 and 6A. The anti-symmetric stretch $v_5$ SO$_4^{2-}$ is much broader than Na$_2$SO$_4$(aq) of comparable sulfate concentration and shows a band contour with peak positions at 1088 cm$^{-1}$, 1127 cm$^{-1}$ and 1158 cm$^{-1}$ and in the broad band at 1109 cm$^{-1}$ for “free” sulfate (compare band contour of Na$_2$SO$_4$(aq) spectra). The measured anisotropic band profile of $v_3$ SO$_4^{2-}$ is shown in Fig. S1† together with the sum curve of the band fit. All these spectroscopic features of the sulfate in La$_2$(SO$_4$)$_3$ solutions lead to the conclusion that sulfate must have penetrated the first hydration shell of La$^{3+}(aq)$ forming a well-defined La$^{3+}$-sulfato complex. In the terahertz frequency range of La$_2$(SO$_4$)$_3$(aq) of a 0.376 mol L$^{-1}$ solution, as mentioned above, the La-O band, of the LaO$_6$ skeleton appears as a broad feature at $\sim$328 cm$^{-1}$ while the fully hydrated, [La(OH$_2$)$_3$]$^{3+}$ occurs at 343 cm$^{-1}$. The downshift of the La$^{3+}$-sulfato complex, [La(OH$_2$)$_3$OSO$_4$]$^{3+}$ compared with the fully hydrated cation was detected in other trivalent-metal sulfate solutions. It should be pointed out that the scattering intensity of the broad La-O features is very small and the solutions are quite dilute. Only in Al$_2$(SO$_4$)$_3$, Ga$_2$(SO$_4$)$_3$, and In$_2$(SO$_4$)$_3$, solutions which are considerably more soluble than La$_2$(SO$_4$)$_3$, and therefore much easier to detect, is such a split into the aqua mode of the fully hydrated species observable without the sulfate and partially hydrated metal-sulfato complex species.$^{8,11,12}$

An overview Raman spectrum of a 0.035 mol L$^{-1}$ La$_2$(SO$_4$)$_3$ solution in heavy water is presented in Fig. S2 (ESI†). The
3.4. Quantitative analysis of sulfato-complex formation in 

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\text{La}_2\text{(SO}_4\text{)}_3\text{(aq)}
\]

The log \(\beta_1\) value for the hydrolysis of \([\text{La(OH}_2\text{)}_3]^3+\) according to:

\[
[\text{La(H}_2\text{O)}_3]^3+ + \text{H}_2\text{O} \leftrightarrow [\text{La(H}_2\text{O)}_4\text{OH}]^2+ + \text{H}_3\text{O}^+ \text{ is at } -8.5 \text{ for } 25^\circ\text{C}.\text{29,30} \text{ Therefore, La}^{3+}(\text{aq}), \text{in contrast to Fe}^{3+}(\text{aq}) \text{ which acts as a strong acid in solution (log } \beta_1 = -2.19 \text{ (ref. 31)) is not markedly hydrolyzed. A 0.01 mol L}^{-1} \text{ La}_2\text{(SO}_4\text{)}_3\text{ solution shows a pH value of 5.53 and therefore the formation of hydrogen sulfate, HSO}_4^- \text{ may be neglected.}

The association between \(\text{La}^{3+}(\text{aq})\) and \(\text{SO}_4^{2-}(\text{aq})\) ions is generally thought to occur via a three step process, referred to as the Eigen mechanism,23,31 in which the strongly hydrated ions combine initially to form an outer-sphere complex. The two interposing water molecules are then lost successively, forming outer-sphere and ultimately inner-sphere complexes. This process is summarized in the following reaction scheme:

\[
\text{La}^{3+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \leftrightarrow \text{La}^{3+}(\text{OH}_2)^{2+} \leftrightarrow \text{La}^{3+}(\text{OH}_3)^{+} \leftrightarrow \text{La}^{3+}(\text{OH}_4)^{0}
\]

where the rate constants for forward \((k_1)\) and backward \((k_b)\) reactions were published from earlier ultrasound absorption measurements.19,20,34,35

The overall association constant, \(K_{\text{La}}\), as measured by traditional techniques such as potentiometry or conductivity, corresponds to the equilibrium:

\[
\text{La}^{3+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \leftrightarrow \text{LaSO}_4^{2-}(\text{aq})
\]

where \(\text{LaSO}_4^{2-}(\text{aq})\) refers to all forms of associated \{\text{La}^{3+}, \text{SO}_4^{2-}\} species of 1 : 1 stoichiometry in aqueous solution (thermodynamics makes no distinction between dissolved species of identical stoichiometry but with differing levels of hydration24,28\). The \(K_{\text{La}}\) value, the overall association constant for the three step mechanism is related to the individual \(K_i\) values via eqn (14):

\[
K_{\text{La}} = K_1 + K_1K_2 + K_1K_2K_3
\]

Three \(K_i\) values were obtained from ultrasound absorption (UA) experiments19,20 namely \(K_1 = 435\), \(K_2 = 1.96\) and \(K_3 = 3.7\). The reported \(K_{\text{La}}\) value, 4200, derived from UA is too large compared with the recommended \(K_{\text{La}}\) value at 3620 at 25°C.26,38

The \(n_1\text{SO}_4^{2-}\) band can be fitted with three band components, a component of the ‘free’ \(\text{SO}_4^{2-}\) (aq) band at \(-980 \text{ cm}^{-1}\), a component at 983 cm\(^{-1}\) representing the \(\text{SO}_4^{2-}\) in the outer-sphere-complex and the mode of the sulfato-complex at 991 cm\(^{-1}\) (Fig. 6B). The sulfato-complex band is quite distinct, while the band of the outer sphere complex is severely overlapped by the \(\text{SO}_4^{2-}\) (aq) band at 980 cm\(^{-1}\). The \(\text{SO}_4^{2-}\) band of the outer-outside sphere complex is not distinguishable from the band of the free sulfate.

The degree of the sulfato-complex formation \(\alpha\), represents the spectroscopically-determined fraction of sulfate present as
sulfato complex according to eqn (8). Fig. 8 shows the present quantitative Raman results as a function of the stoichiometric La₂(SO₄)₃ concentration at 23 °C. The band of the sulfate band, the so called bound sulfate, and the degree of sulfato-complex formation of the equilibrium reaction > 0.003 mol L⁻¹ but below this concentration vanishes more severely. This paradox can be resolved if it is assumed that the inner-sphere complex, [La(OSO₃)]⁺ is in equilibrium with the outer-sphere complex, [La(OH₂)SO₄]⁺ and not with the “free” sulfate. The Raman spectroscopically determined Kₜ value was determined according to eqn (12). In Table S1 (ESI†) the data of the analytical curve fitting on the r₁-SO₄²⁻ band profile of the two band components at 981 cm⁻¹ and 991.1 cm⁻¹ are given such as integrated band intensities, A₉₈₁ and A₉₉₁, as well as the degree of sulfato-complex formation of the equilibrium between the outer-sphere complex and the inner-sphere-sulfato complex. From these data a Kₜ-value was determined at 0.90 ± 0.1 at 23 °C and it appears that the Raman derived Kₜ value is comparable to the UA-values considering the uncertainty of the data from the UA measurements.¹⁹,²⁰,³⁴,³⁵

**Temperature dependent measurements.** A 0.0094 mol L⁻¹ La₂(SO₄)₃ solution was measured from 23 to 98 °C and the temperature dependent isotropic scattering profiles are given in Fig. 9. Generally, the peak position of the r₁-SO₄²⁻ band complex shifts to slightly lower wavenumbers with temperature increase. The band of “free” sulfate at 23 °C peaks at 981.0 cm⁻¹ and shifts to 976.5 cm⁻¹ at 98 °C. A similar peak shift was observed for the band of the coordinated sulfate which peaked at 991 cm⁻¹ at 23 °C and shifts to 987 cm⁻¹ at 98 °C. Furthermore, the band complex (and the band components) broadens with temperature. In addition to these two already resolved band components a third band component assigned to sulfato of the outer-sphere ion pair, La³⁺(H₂O)SO₄²⁻ was detected at 983 cm⁻¹ at 23 °C which shifted to 978.6 cm⁻¹ at 98 °C. The results of a three component band fit on the r₁-SO₄²⁻ band complex are given in Table S2 (ESI†). The most striking fact, however, is the rise of the band component of the coordinated sulfate band, the so called bound sulfate, and the degree of sulfato-complex formation rises from 0.25 at 23 °C to 0.42 at 98 °C.

The increase of the La³⁺–sulfato complex with enhancing temperature shows that the rate determining third step of reaction (10) is an endothermic process by which heat is absorbed, making the enthalpy change positive. The change of the equilibrium constant as a function of temperature follows the equation:

\[
\ln(Kₜ) = -\frac{ΔH^0}{RT} + \frac{ΔS^0}{R}.
\]

Plotting ln Kₜ as a function of 1/T and assuming that the change of the heat capacity in this small temperature range is zero leads to the enthalpy and the entropy of the last step of the sulfato-complex formation, the outer-sphere, inner-sphere sulfato complex formation according to La³⁺(OH₂)SO₄²⁻ → La³⁺OSO₃²⁻. The following quantitative results were derived from the temperature-dependence of ln(Kₜ) as a function of the reciprocal temperature (in Kelvin): ΔH° = 18.6 kJ mol⁻¹ and ΔS° = 62.1 J mol⁻¹ K⁻¹. The enthalpy for the rate determining step of eqn (9) compares favorably with the extrapolated value, 15 kJ mol⁻¹, for ΔH° taken from ref. 39.

Finally, it should be mentioned that Malatesta and co-workers showed, by comparing activity coefficient data on
La$_2$(SO$_4$)$_3$(aq) and La(ClO$_4$)$_3$(aq), that in the sulfate system of La$^{3+}$ “there is evidence of short-range interactions that add to long-range interactions for lanthanum and bivalent metal sulfates, as if sulfate ions were displacing water from the hydration shells of the cations”. This is exactly what the Raman spectroscopic data show.

4. Conclusions

Raman spectroscopic measurements have been made of aqueous solutions of La(ClO$_4$)$_3$, La$_2$(SO$_4$)$_3$, and Na$_2$SO$_4$ in water and heavy water, in the terahertz frequency region (40–1400 cm$^{-1}$) and down to low concentrations (0.000263 mol L$^{-1}$). Temperature dependent measurements have been carried out on a 0.0098 mol L$^{-1}$ La$_2$(SO$_4$)$_3$ solution from 23–98°C. In solutions of La(ClO$_4$)$_3$ with water and heavy water, the [La(OH$_2$)$_3$]$^{3+}$ and [La(OD$_2$)$_3$]$^{3+}$ have been characterized and a weak, strongly polarized band observed at 343 cm$^{-1}$ and 326 cm$^{-1}$ respectively assigned to the $v_1$ LaOH$_3$ mode, the breathing mode of the clusters. The Raman spectroscopic data suggest that the [La(OH$_2$)$_3$]$^{3+}$ ion is thermodynamically stable in dilute perchlorate. No inner-sphere complexes in these dilute solutions could be detected spectroscopically.

In La$_2$(SO$_4$)$_3$(aq), in addition to the $v_1$SO$_4^{2-}$ mode at 980 cm$^{-1}$, a pronounced band component at 991 cm$^{-1}$ has been assigned to an inner-sphere complex (ISC). The sulfate is most likely bound as a monodentate ligand ([La(OSO$_4$)]$^-$). Conformation of this assignment is provided by the component at 312 cm$^{-1}$ of the [La(OH$_2$)$_3$]OSO$_4$$^-$ unit in addition to the band at 343 cm$^{-1}$ for the fully hydrated cluster, [La(OH$_2$)$_3$]$^{3+}$. A similar $v_1$SO$_4^{2-}$ band contour has been observed in La$_2$(SO$_4$)$_3$ solutions in heavy water. After subtraction of the component of the ISC at 991 cm$^{-1}$, the $v_1$SO$_4^{2-}$ band in La$_2$(SO$_4$)$_3$(aq) showed systematic differences from that in (NH$_4$)$_2$SO$_4$(aq) and dilute Na$_2$SO$_4$(aq).

This is consistent with a $v_1$SO$_4^{2-}$ band at 983.3 cm$^{-1}$ that can be assigned to the existence of an outer-sphere complex ion (OSCs). The band profile of the weaker antisymmetric S–O stretching mode, $v_2$SO$_4^{2-}$ shows asymmetry and has been fitted with four band components including the component of the “free” $v_2$SO$_4^{2-}$ band reinforcing the existence of the ligated sulfate. In aqueous La$_2$(SO$_4$)$_3$ solutions thermodynamically stable ISC have been detected down to very low concentrations at 0.00026 mol L$^{-1}$ and in addition an OSC, [La(OH$_2$)$_3$]OSO$_4^-$ and the free non-ligated sulfate. The observed change of the equilibrium concentration of the ISC, ([LaSO$_4^-$]) with dilution reflects the stepwise sulfato-complex formation. A $K_r$-value has been determined at ~0.9 of the equilibrium between OSC and ISC.

Temperature dependent measurements (23–98°C) on a 0.0098 mol L$^{-1}$ La$_2$(SO$_4$)$_3$ solution has shown that the concentration of the La$^{3+}$ sulfato-complex rises with increasing temperature while at the same time the concentration of the “free” sulfate diminished. The sulfato-complex formation is an endothermic process absorbing heat with increasing temperature. The following thermodynamic parameters for the rate determining equilibrium, [La(OH$_2$)$_3$SO$_4^-$] $\leftrightarrow$ [LaOSO$_4^-$] + H$_2$O, has been determined: $\Delta H^0 = 18.6$ kJ mol$^{-1}$ and $\Delta S^0 = 62.1$ J mol$^{-1}$ K$^{-1}$.

References


