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Raman Spectroscopic Studies of Scandium(III) Hydration in Aqueous Solution – about the First Hydration Sphere of Sc(III) in Solution

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It has been shown conclusively that Sc(III) in aqueous perchlorate solution occurs as an hexaaqua cation. The weak, polarized Raman band assigned to the $v_1(a_{1g})$ ScO₆ mode of the hexaaqua-Sc(III) ion (T_h symmetry for the whole complex ion or O_h symmetry for the ScO₆ unit) has been studied as a function of concentration and temperature. The isotropic scattering geometry in R-format was employed in order to measure the true vibrational contribution of the band and account for the Boltzmann temperature factor B and the wavenumber factor v. The $v_1(a_{1g})$ ScO₆ mode at 442 cm⁻¹ of the hexaaqua-Sc(III) shifts only 3 cm⁻¹ to lower wavenumbers and broadens about 20 cm⁻¹ for a 60 °C temperature increase. The Raman spectroscopic data suggest that the hexaaqua Sc(III) ion is stable in perchlorate solution within the temperature range measured.

Besides the polarized component at 442 cm⁻¹, two weak depolarized modes at 295 cm⁻¹ and 410 cm⁻¹ were measured in the Raman effect. These two modes of the ScO₆ unit were assigned to $v_5(f_{2g})$ and $v_2(e_g)$ respectively. The infrared active mode, $v_3(f_{1u})$, was measured to be at 460 cm⁻¹. The wavenumber data confirm the centrosymmetry of the Sc(III)aqua-complex, in opposite to earlier Raman results.

These findings are also in contrast to the results found in $Sc_2(SO_4)_3$ solutions, where sulfate replaces water in the first hydration sphere and forms quite strong sulfato complexes. In ScCl₃ solutions weak chloro-complex(es) could be detected.

1. Introduction

In the last two decades, many experimental studies using X-ray and neutron scattering have been carried out to describe the hydration structure of nearly

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all stable metal ions. Despite great research effort and its fundamental importance, the first hydration number of Sc(III) in aqueous solution is still an open question (cf. data in [1, 2]). Raman spectroscopic results [3] and a recent X-ray absorption fine structure measurement [4] proposed a probable first hydration number of 7. It is known that Sc(III) is quite similar to Al(III) because of its small ionic radius (~0.73 Å) [5]. In solid state, oxygencoordinated Sc(III) compounds occur in coordination numbers equal to three, six, seven, eight and nine, with the six coordination being the most common (octahedral or trigonal prism), whilst the next common type is the eight coordination (cubic, square antiprism and dodecahedral coordination polyhedron) [6]. The average Sc(III)-O bond length is 2.11 Å for the six coordination and 2.24 Å for the eight coordination. The results of a recent crvstal structure of scandium(III) trifluoromethan enneahydrate $[Sc(OH_2)_0(CF_3SO_3)_3]$ [7] reveal that Sc^{3+} is surrounded by 9 water molecules (tricaped trigonal prism) with six short Sc³⁺-O bonds (2.171 Å) and three longer bonds (2.47 Å). 1-H-NMR measurements [8] on Sc(III)-perchlorate and -nitrate in water-acetone mixtures were carried out, but the coordination number of the first hydration sphere could not be detected because of the rapid proton exchange between bulk and water in the first coordination sphere, even at -100 °C for perchlorate solutions. In nitrate solutions unusually low hydration values of 3.9 to 5.1 were detected, which clearly indicated that hydrolysis and nitrato complex formation were important in this solution. Kanno and co-workers [3] measured the Raman spectra of aqueous Sc³⁺ and Al³⁺ chloride solutions in vitreous state in order to avoid the interference of the strong quasi elastic Rayleigh wing, which extends well over 500 cm⁻¹ and prohibits the clear detection of weak low wavenumber modes of metal aqua ions.

Raman spectroscopy has been extensively used to elucidate the spectroscopic characteristics of cations in aqueous solutions. However, in solution, the strong quasi elastic Rayleigh wing prohibits the clear detection of the weak low wavenumber modes of the metal aqua ions [9]. To circumvent this difficulty, Raman difference spectroscopy has been developed [10, 11]. The subtraction of a synthetic background has also been employed to obtain baseline corrected Raman spectra [12-14].

It is well known that dissolved ions (especially anions) alter the low wavenumber Raman spectrum of water [15]. Therefore, the Raman difference spectra obtained by subtracting the spectrum of pure water from the spectrum of an aqueous solution must be viewed with caution as pointed out in previous papers [9, 16]. On the other hand, it is not necessary to employ Raman difference spectroscopy or to subtract a synthetic Rayleigh wing from the aqueous electrolyte spectra in order to obtain baseline corrected spectra. It has been shown [17-19] that for accurate relative intensity measurements it is essential to normalize the low wavenumber Raman data for the Bose-Einstein temperature factor, B, and a wavenumber factor in

order to present the data in a spectral form that is directly related to the relative molar scattering factor, $S_Q(\bar{\nu}) \propto (\partial \alpha / \partial Q_i)^2$, where Q_i is the mass-weighted normal coordinate.

The reduced or $R_Q(v)$ spectrum was constructed after Eq. (1):

$$\mathbf{R}_{\mathbf{0}}(\overline{\nu}) = \mathbf{I}(\overline{\nu}) \cdot (\overline{\nu}_{\mathbf{0}} - \overline{\nu}_{\mathbf{i}})^{-4} \cdot \overline{\nu}_{\mathbf{i}} \cdot \mathbf{B}$$
(1)

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Equation (1) is valid under the condition that the normal coordinates are taken to be harmonic and the polarizability expansion is terminated after the first-order term (i.e. the double harmonic approximation). The $R_Q(\bar{\nu})$ spectrum has been related to the vibrational density of states spectrum and may also be considered as the energy absorbed in a scattering process (see [17–19] and references therein).

In this study, Raman spectra of scandium perchlorate, chloride and sulfate solutions were obtained as a function of concentration in order to draw conclusions about the stability of its aqua complex. It is well known that perchlorate does not penetrate the first hydration sphere, which allows a vibrational characterization of the aqua-scandium species. In scandium chloride solutions, the situation is not so clear, because of possible chloro complex formation [20], though Kanno *et al.* [3] stated that chloride does not penetrate the first hydration sphere of scandium(III).

2. Experimental section, data treatment and *ab initio* calculations

The Sc(ClO₄)₃ stock solution was prepared by dissolving Sc₂O₃ with a slight excess of HClO₄. The solution contains an excess of ca. 10% HClO₄ in order to prevent deprotonation of Sc(III). The density of the solution was determined with a standardized 5 ml pycnometer at 20 °C. The Sc(III) content of the solution was determined by colorimetric titration with standard EDTA and xylenol orange as an indicator [21]. The solution pH was measured with a glass electrode and was ca. 0.8. The perchlorate concentration was determined by passing a portion of a solution through a column with a strong cation exchanger (Dowex 50W-X8) and titrating the eluate with standardized NaOH solution. The Sc(ClO₄)₃ stock solution was 1.65 mol/L (1.905 mol/kg) with an excess of 10% HClO₄. A deuterated solution was prepared by dissolving the Sc(ClO₄)₃ in D₂O (Cambridge Isotope Laboratories, 99.9%) and evaporating the water off in a vacuum distillation apparatus. This process was repeated three times. The deuteration grade, checked by Raman spectroscopy, (in the OD and OH region) was better than 99.9%.

The ScCl₃ stock solution was prepared by dissolving Sc_2O_3 with an excess amount of aqueous HCl solution. The solution was analysed for scandium by colorimetric titration with standard EDTA [21]. The chloride content was determined with a standardized AgNO₃ solution after the

method by Fajans [22]. The solution densities was determined with a pycnometer (5 ml) at 20 °C. The stock solution was 2.550 mol/L (2.801 mol/ kg) and contained an excess of 10% HCl to prevent hydrolysis. With the ScCl₃ stock solution and a LiCl stock solution, we prepared a ScCl₃ solution with excess chloride (as LiCl) by weight. The mole ratio in the solution was found to be ScCl₃:LiCl:H₂O = 0.01428:0.10594:0.8798; e.g. a mol ratio of Sc(III):Cl(I) = 1:10.4.

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A $Sc_2(SO_4)_3$ stock solution was prepared by dissolving Sc_2O_3 with sulfuric acid and recrystallizing the $Sc_2(SO_4)_3 \cdot 5 H_2O$ twice. Sc(III) was determined as described above and the sulfate content was checked by titration with standardized $Ba(ClO_4)_2$ solution using Thorin (2-(2-dihydroxy-3,6-disulfo-1-naphthylazo) benzene arsonic acid) as an adsorption indicator [22]. Before titration, the solution was passed through a column with a cation exchanger (Dowex 50W-X8). The eluate was then titrated with the standardized $Ba(ClO_4)_2$ solution and this elution technique prevented co-precipitation of Sc(III) with $BaSO_2$ [22]. The stock solution was 0.98 mol/L and contained an excess of ca. 1.0% sulfuric acid. Density and pH were checked as described above.

Great care was taken to characterize the solutions in order to be sure about possible processes occurring in the solutions, like complexation, hydrolysis and precipitation of basic salt [23, 24].

All solutions were filtered through a 0.22 micron Millipore filter into a 150 mm ID quartz tube before Raman spectroscopic measurement.

Raman spectra were obtained with a Coderg PHO Raman spectrometer using the 488.0 and 514.5 nm argon ion laser line with a power level at the sample about 0.9 W. The slit widths of the double monochromator were set normally at 1.8 cm⁻¹. The scattered light was detected with a PMT cooled to -20 °C, integrated with a photon counter and processed with a box-car averager interfaced to a personal computer. Two data points were collected per wavenumber. To increase the signal-to-noise ratio six data sets were collected for each scattering geometry (I_{II} and I_⊥). A quarter wave plate before the slit served to compensate for grating preference. I_{II} and I_⊥ spectra were obtained with fixed polarization of the laser beam by rotating the polaroid film at 90° between the sample and the entrance slit to give the scattering geometries:

$$I_{\parallel} = I(Y[ZZ]X) = 45 \,\bar{a}'^2 + 4 \,\gamma'^2 \tag{2}$$

$$I_{\perp} = I(Y[ZY]X) = 3\gamma^{\prime 2}.$$
(3)

The isotropic spectrum is then formed:

$$\mathbf{I}_{\rm iso} = \mathbf{I}_{\parallel} - 4/3 \cdot \mathbf{I}_{\perp} \tag{4}$$

and of course the isotropic spectrum can also be formed in the R expression:

$$\mathbf{R}_{\rm iso} = \mathbf{R}_{\parallel} - 4/3 \cdot \mathbf{R}_{\perp} \,. \tag{5}$$

Further spectroscopic details about the high temperature measurement, the band fit procedure and details about R normalized Raman spectra are described in previous publications [16].

For quantitative measurements, the perchlorate band, v_1 -ClO₄⁻ at 935 cm⁻¹ was used as an internal standard. From the R_{iso} spectra, the relative isotropic scattering coefficient S(v_1 ScO_n) was obtained. The use of S values instead of J values has the advantage that these relative scattering coefficients can be put on an absolute scale if an absolute standard reference is considered. For further details about S-values cf. [16a].

3. Experimental results and discussion

3.1 Raman spectroscopic results

3.1.1 $Sc(ClO_4)_3$ solution

Raman spectra of a 1.65 M Sc(ClO₄)₃ solution were analysed between 60 and 1300 cm⁻¹. The "free" ClO₄ ion possesses T_d-symmetry and has nine modes of internal vibrations spanning the representation $\Gamma_{vib}(T_d) = a_1 + e$ $+ 2 f_2$. All modes of vibration are Raman active but in i.r. only the f₂ modes are active. The spectrum of a 1.65 M Sc(ClO₄)₃ solution shows the predicted four Raman-active bands for the tetrahedral ClO₄. An overview Raman spectrum in R_{pol} format at 25 °C is given in Fig. 1a and in Fig. 1b the expanded wavenumber region from 60–700 cm⁻¹ is given. The v₁-ClO₄ band centred at 935 cm⁻¹ is totally polarized, whereas v₃(f₂)-ClO₄ centred at 1114 cm⁻¹ is depolarized as are the deformation modes v₄(f₂)-ClO₄ at 630 cm⁻¹ and v₂(e)-ClO₄ at 463 cm⁻¹ [25]. In Fig. 2a overview Raman spectrum of a 1.65 M Sc(ClO₄)₃ solution in the wavenumber range from 50–4400 cm⁻¹ is presented.

Besides the perchlorate modes, a mode at 442 ± 2 cm⁻¹ (fwhh = 74 ± 2 cm⁻¹) becomes visible in the isotropic Raman spectrum. In addition to this isotropic mode, a weak broad depolarized mode at 295 ± 5 cm⁻¹ is visible. A very weak mode at 410 ± 5 cm⁻¹ can be observed in the crystalline powder of Sc(ClO₄)₃ · 6 H₂O, which is overlapped in aqueous solution spectra. These spectroscopic findings suggest a hexaaqua Sc(III) ion in perchlorate solution and the isotropic band at 442 cm⁻¹ can be assigned to $v_1(a_{1g})$ ScO₆ and the depolarized band at 295 cm⁻¹ can be assigned to $v_2(e_g)$ ScO₆. It should be noted here, that in ScCl₃ solutions a band near 300 cm⁻¹ (precisely at 306 cm⁻¹) appears, which is polarized and obscures the depolarized mode at 295 cm⁻¹ cannot be found in the





Fig. 1a. Polarized Raman spectrum in R-format of a $1.65 \text{ M Sc}_2(\text{ClO}_4)_3$ solution in the wavenumber region between $55-1300 \text{ cm}^{-1}$ at 25 °C.



Fig. 1b. Raman spectra (R_{pol} , R_{depol} and R_{iso}) of a 1.65 M Sc₂(ClO₄)₃ solution in the wavenumber region between 55–750 cm⁻¹ at 25 °C. Note the isotropic component at 442 cm⁻¹, which has been assigned to $v_1(a_{1g})$ ScO₆, and the depolarized band at 295 cm⁻¹ has been assigned to $v_5(f_{2g})$ ScO₆. The weak depolarized band at 410 cm⁻¹ has been assigned to $v_2(e_g)$ ScO₆.





Fig. 2. Overview Raman spectrum (R_{iso}) of a 1.65 M Sc₂(ClO₄)₃ solution in the wavenumber region between 55–4200 cm⁻¹ at 25 °C.

 $Sc(ClO_4)_3$ solutions (the perchlorate solutions used were proofed to be free of chloride!). A Raman spectrum of the $Sc(ClO_4)_3 \cdot 6 H_2O$ at 25 °C reveals the weak depolarized modes quite clearly.

Kanno *et al.* have interpreted their Raman spectroscopic data in $Sc(ClO_4)_3$ solution with a hepta-aqua Sc(III) cluster. A hepta-aqua Sc(III) cluster with its ScO_7 unit possesses C_2 symmetry. The 18 normal modes span the representation $\Gamma_v(C_2) = 9 \cdot a(Ra, i.r.) + 9 \cdot b(Ra, i.r.)$. All doubly and triply degenerate modes would loose their degeneracy and split. Certainly this is not the case. Furthermore all modes would have to be Raman and infrared active, which is also not observable. It is not clear at all why a band at 300 cm⁻¹ (its depolarization ratio could not be dedected) should speak for a hepta-aqua species. It could be shown, that the mode at 295 cm⁻¹ is depolarized in $Sc(ClO_4)_3$ solution and appears polarized in $ScCl_3$ solution at 306 cm⁻¹. The spectra of $ScCl_3$ solutions will be dealt with in the next section.

The isotropic mode shifts with deuteration of the $Sc(ClO_4)_3$ solution to 417 cm⁻¹ in accordance with expected isotope shift:

$$v_1[(\mathrm{Sc}(\mathrm{OD}_2)_6^{3+}] = \sqrt{18.02/20.03} \cdot v_1[(\mathrm{Sc}(\mathrm{OH}_2)_6^{3+}] = 0.948 \cdot 442 \text{ cm}^{-1} = 419 \text{ cm}^{-1}.$$
(6)

Table 1. The ScO₆ skeleton modes (ScO₆ unit possesses O_h symmetry), Raman and i.r. spectroscopic frequencies in aqueous Sc(ClO₄)₃. (In ScCl₃, Sc(NO₃)₃ and Sc₂(SO₄)₃ solutions complex formation occurs.)

Assignment and activity	Exper. wavenumbers (cm $^{-1}$) in H ₂ O
$ \frac{v_1(a_{1g}) \text{ Ra}}{v_2(e_g) \text{ Ra}} \\ v_3(f_{1u}) \text{ i.r.} \\ v_4(f_{1u}) \text{ i.r.} \\ v_5(f_{2g}) \text{ Ra} \\ v_6(f_{2u}) - $	442 ± 1 (0.003) 410 ± 5 (0.75) $460\pm5^{*}$ not observed 295 ± 5 (0.75) not active

* D. M. Adams, Metal-Ligand vibrations and related vibrations, E. Arnold, London (1967).

Relative intensity measurements for three different $Sc(ClO_4)_3$ solutions as a function of concentration (1.65 mol/L, 1.00 mol/L and 0.5 mol/L) yield a relative scattering coefficient for the v_1 Sc-O mode, $S_h = 0.034 \pm 0.002$. The perchlorate band, $v_1(a_1)ClO_4^-$ at 935 cm⁻¹, served as reference band. The S_h value is defined as the corrected relative scattering efficiency of the $[M(OH_2)_n]^{m+}$ aqueous metal hydrates. Furthermore, S_h is defined in the pure isotropic R-spectrum. For the v_1 Al-O mode a S_h value of 0.02 was found, for the v_1 Ga-O mode a value of 0.09 and for v_1 In-O a value of 0.15 reflecting the increase in the softness of these group IIIa metal ions with increase in the periodic number. Sc(III), as the first representative of group IIIb metal ions, shows a slightly higher relative molar scattering coefficient than Al(III). This means, in the terminology of inorganic chemistry, Sc(III) is a hard cation.

The infrared active mode, $v_3(f_{1u})$ was measured to be at 460 cm⁻¹ (taken from ref. 26). The infrared active mode, $v_3(f_{1u})$, at 460 cm⁻¹ confirms the centrosymmetry of ScO₆. The wavenumbers of the ScO₆ unite and the assignments of the modes are presented in Table 1.

These findings are in contrast with the results reported by Kanno *et al.* [3a] who reported four Raman bands in $ScCl_3$ and $Sc(ClO_4)_3$ solutions and vitreous state at liquid nitrogen temperature. In light of these findings, the question arises: why are there four Raman bands in vitreous $ScCl_3$ solution as quoted in [3a]? The answer can be found by inspecting the $ScCl_3$ solution spectra, which are given below.

3.1.2 ScCl₃ solution

The Raman spectra of a 2.55 M ScCl₃ stock solution at 25 °C is presented in Fig. 3. In the isotropic Raman spectrum three bands are observable: 436 cm^{-1} (FWHH = $80\pm2 \text{ cm}^{-1}$), 306 cm^{-1} (FWHH $30\pm2 \text{ cm}^{-1}$) and weak broad band 200 cm⁻¹ (FWHH ca. 120 cm⁻¹) representing the inter-





Fig. 3. Raman spectra (R_{pol} , R_{depol} and R_{iso}) of a 2.55 M ScCl₃-solutions in the wave-number region between 55–750 cm⁻¹ at 25 °C.

molecular mode of H-bonded Cl⁻ ions of the form $H-O-H\cdots Cl^{-}$ [27, 28] (the possibility that a weak Sc-Cl mode is overlapped by the restricted intermolecular mode cannot be excluded, further investigations of the ScCl₃-water system is necessary). The band at 436 cm⁻¹ shows also a shoulder at the low wavenumber side at ca. 420 cm⁻¹. With dilution of ScCl₃ the band at 306 cm⁻¹ disappears gradually and in the 0.255 M ScCl₃ solution it is almost gone as can be seen in Fig. 4. We can therefore conclude that the band at 306 cm⁻¹ is due to a $Sc^{3+}-Cl^-$ mode of $Sc(OH_2)_{6-n}Cl_n^{+(3-n)}$ and the mode 436 cm⁻¹ represents the Sc-aqua mode of uncomplexed and complexed Sc(III). That the mode at 306 cm^{-1} is due to Sc³⁺-Cl⁻ becomes clear by inspecting Fig. 5, in which a ScCl₃ solution with an excess of LiCl (Sc(III): Cl(I) = 1: 10.4) is presented. The isotropic mode at 306 cm⁻¹ is now dominant and the mode of the Sc-hexaaqua ion, v_1 ScO₆, disappeared completely, whilst a medium strong band at 425 cm⁻¹ occurs, which can be assigned to the vibrations of the remaining water ligands in the mixed Sc-chloro water complex, most likely trans- $ScCl_2(OH_2)_4^+$. It should be noted that the $Sc^{3+}-Cl^-$ mode in the $ScCl_3$ -LiCl mixture is not shifted (though the chloride excess is high) compared to the ScCl₃ solution series and suggests that the excess in chloride did not result in formation of a Sc(III) complex with a higher chloride/Sc(III) ratio (like $ScCl_6^{3-}$, which is known in crystalline form; e.g. Cs_3ScCl_6 [29, 30]. The





Fig. 4. Isotropic Raman spectra of a dilution series of $ScCl_3$ (2.55 M, 1.55 M and 0.255 M $ScCl_3$ -solutions from top to bottom) at 25 °C.



Fig. 5. Isotropic Raman spectrum of a ScCl₃-LiCl-water mixture at 25 °C. Note the modes at 306 cm⁻¹ and the weaker, broader mode at 425 cm⁻¹.

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same principal findings were made during the course of our Raman spectroscopic studies on electrolyte systems, namely Al(III)-, Ga(III)- and In(III)perchlorate, chloride and sulfate aqueous solution. Whilst in perchlorate solutions the hexaaqua ions are stable, in chloride solutions only Al(III) hexaaqua ions are stable. In Ga(III) and In(III) solutions chloro complexes are formed [40]. It is known that excess chloride in a GaCl₃ solution results in formation of GaCl₄⁻ from species Ga(OH₂)_{6-n}Cl_n⁺⁽³⁻ⁿ⁾ (n = 1 or 2) [31, 32]. The mode, v_1 GaCl₄⁻, is quite distinct from the mode, v Ga³⁺-Cl⁻, in the Ga(OH₂)_{6-n}Cl_n⁺⁽³⁻ⁿ⁾ (n = 1 or 2) species [31, 32]. Obviously, in ScCl₃ solutions (even with excess of Cl⁻) no species like ScCl₄⁻ and ScCl₆³⁻ are formed.

The coordination of Sc(III) by chloride in aqueous solution was also studied with non spectroscopic methods initially by Paul [33] and the species ScCl²⁺ and ScCl² were invoked. For 25 °C and an ionic strength of 0.5 M the equilibrium quotients for the reactions $Sc^{3+} + Cl^{-} = ScCl^{2+}$ and $ScCl^{2+} + Cl^{-} = ScCl_{2}^{+}$ were found to be 11.7 and 10.9. Later investigations [34, 35] indicated the presence of these species although the stability constant derived differ considerably from those reported by Paul. Scandium(III) is slightly adsorbed by an anion exchanger column from 7 to 12 M HCl indicating the presence of an anionic species at high chloride concentration [36]. From an ionophoretic investigation by Šmirous et al. [37] invoked the electro neutral ScCl₃ species and ScCl₄ in ScCl₃ solutions with excess of Cl⁻. It should be mentioned that these physicochemical methods detect besides the inner-sphere complex also a complex of an outer-sphere type. Raman spectroscopy, on the other hand, allows a characterization of the inner-sphere complexes. In recent publications by Rudolph et al. [38] it was shown that in transition metal-sulfate solutions the majority of the complexes at room temperature are of the outer-sphere type. A recent EXAFS study revealed that chromochloroaqua complexes, $[CrCl_n(OH_2)_{6-n}]^{(3-n)+}$ (n = 1-3) form outer-sphere complexes with chloride [39].

Our spectroscopic results show clearly chloro complex formation in $ScCl_3$ solutions (of both types), in direct contrast to the findings by Kanno *et al.* [3]. Therefore, the spectrum of Sc(III) in perchlorate solution is consistent with an hexaaqua cation.

3.1.3 $Sc_2(SO_4)_3$ solution

When a polyatomic anion like sulfate replaces water in the first coordination sphere of the cation, marked changes occur in the spectrum of the ligated sulfate, so that it is possible to differentiate between the bands of the ligated and the unligated sulfate. Additionally, a shift or splitting of the metal aqua modes and the appearance of a metal-ligand vibration at low wavenumbers $(100-300 \text{ cm}^{-1})$ should be detectable. For these reasons, the unligated sul-





Fig. 6. Raman spectra (R_{pol} , R_{depol} and R_{iso}) of a 0.98 M Sc₂(SO₄)₃ solution in the wavenumber region between 60–750 cm⁻¹ (top) and 800–1300 cm⁻¹ (bottom) at 25 °C.

fate in the $(NH_4)_2SO_4$ -H₂O system was studied so that information about the "free" sulfate could be obtained [38]. These data on "free" sulfate can then be compared to sulfate in $Sc_2(SO_4)_3$ solution.





The "free", undistorted SO_4^{2-} ion in Raman spectra of aqueous $(NH_4)_2SO_4$ -solution $(T_d$ -symmetry) has nine modes of internal vibrations having the representation $\Gamma_{vib}(T_d) = a_1 + e + 2 f_2$. All modes of vibration are Raman active but in i.r. only the f_2 modes are active.

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The spectral details for the tetrahedral SO₄²⁻ in (NH₄)₂SO₄-solution may be found in [38]. The $v_1(a_1)$ -SO₄²⁻ band centred at 981.4 cm⁻¹ is polarized ($\rho = 0.006$) whereas $v_3(f_2)$ -SO₄²⁻, centred at 1110 cm⁻¹, and the deformation modes $v_4(f_2)$ -SO₄²⁻ at 617 cm⁻¹ and $v_2(e)$ -SO₄²⁻ at 452 cm⁻¹, are depolarized. In $Sc_2(SO_4)_3$ solutions, strong sulfato complexes are formed (strong in the thermodynamical sense). Fig. 6 shows the Raman spectrum of the 0.98 M stock solution of $Sc_2(SO_4)_3$. Besides the modes for 'free' SO_4^{2-} in the stretching region (800-1300 cm⁻¹) the following modes, corresponding to ligated sulfate could be detected: 1000 cm⁻¹, 1010 cm⁻¹, 1030 cm⁻¹, 1124 cm^{-1} , 1130 cm^{-1} , 1158 cm^{-1} and 1220 cm^{-1} . In the bending region the following modes could be detected: 660 cm⁻¹, 623 cm⁻¹, 608 cm⁻¹, 514 cm⁻¹, 460 cm⁻¹, 445 cm⁻¹, 416 cm⁻¹, 290 cm⁻¹ and 190 cm⁻¹. The v_1 ScO₆ mode of the Sc(III)-hexaaqua ion has completely disappeared and a new isotropic component at 290 cm⁻¹ has occurred, indicating that in $Sc_2(SO_4)_3$ solutions from 0.98 M to 0.098 M all Sc^{3+} occur as sulfato complexes (inner-sphere) of, until now, unknown origin. From the complexity of the spectrum it can be deduced that at least three complex species occur and with dilution the complexes dissociate into sulfate and Sc3+-hexahydrate. The Sc-hexahydrate itself shows pronounced hydrolysis with dilution and at ca. 0.004 M insoluble basic Sc oxyhydrate precipitates. The results of our dilution studies of $Sc_2(SO_4)_3$ will be published in a forthcoming paper, but in the context of this paper, it is worthwhile to state the fact that in contrast to $Al_2(SO_4)_3$ solution, Sc(III) forms strong sulfato complexes. Our results on $Al_2(SO_4)_3$ were published in [40]. It should be noted that 17-O NMR results [41] showed that Al(III) is not only a thermodynamically stable ion but also kinetically quite inert (first order rate constant = 0.13 sec^{-1}), whilst Sc(III) is thermodynamically the stable ion in aqueous solution but kinetically labile [42], which means the water exchange is fast (ca. $5 \cdot 10^7$ sec⁻¹). Whilst in concentrated Al₂(SO₄)₃ solutions the sulfato complex formation is weak (thermodynamically) and the sulfato complex formation in $Sc_2(SO_4)_3$ solution is strong. The tendency to form sulfato complexes is somewhat different, since at room temperature the degree of sulfato complex formation is small in $Al_2(SO_4)_3$ solution (ca. 15%) whilst in $Sc_2(SO_4)_3$ solution sulfato complexes are the dominant species.

3.1.4 Al(III) in aqueous solution

In contrast to Sc³⁺, Al³⁺ forms hexaaqua ions [40] in aqueous, Al(ClO₄)₃, AlCl₃ and Al(NO₃)₃ solutions. In these solutions the only Al(III) species observable is the [Al(OH₂)³⁺₆] as revealed by their solution spectra [40]. A





Fig. 7. Raman spectra (R_{pol} , R_{depol} and R_{iso}) of a 2.85 M AlCl₃ solution in the wavenumber region between 70–1300 cm⁻¹ at 25 °C. The insert gives the spectra (R_{pol} , R_{depol} and R_{iso}) of a slightly over saturated AlCl₃ solution (ca. 3.40 M) in the extended wavenumber region 240–650 cm⁻¹.

complete vibrational analysis of the well characterized $[Al(OH_2)_6]^{3+}$ ion is given in [40a, b]. It should be mentioned that the vibrational analysis sees the water as a point mass, so the symmetry of the complex ion becomes O_h. In Fig. 7 the Raman spectrum of a AlCl₃ solution Raman spectrum is given and in Table 2 the experimental wavenumbers of the Al(III) hexaaqua ion are presented.

3.1.5 General comparisons of Sc(III) with group IIIA metal ions, transition metal ions and lanthanides

It is generally thought that Sc(III) is similar to Al(III) because of its small ionic radius [43], but for certain properties, the similarity to yttrium and the lanthanides is also visible [43]. Scandium behaves in many respects, as a typical first transition metal ion rather than a lanthanide [44]. In scandium(III), the 4s and 3d orbitals are both energetically accessible, which would make it like the transition metals. The electronic configuration of Sc(III) ion is just the [Ar] core $(1s^2 2s^2 2p^6 3s^2 3p^6)$, and there are no delectrons which make the chemistry of the transition metals so interesting. The chemistry of scandium is also similar to the lanthanides because the

Table 2. The AlO₆ skeleton modes (AlO₆ unit possesses O_h symmetry), Raman and i.r. spectroscopic frequencies in aqueous Al(ClO₄)₃, AlCl₃ and Al(NO₃)₃ solutions. (In these solutions no inner-sphere complexes are formed, whilst in Al₂(SO₄)₃ solutions formation of sulfato complexes occurs.)

Assignment and activity	Exper. wavenumbers (cm^{-1}) in H_2O	Exper. wavenumbers (cm^{-1}) in D_2O
$\begin{array}{c} \hline & \\ \hline v_1(a_{1g}) & Ra \\ v_2(e_g) & Ra \\ v_3(f_{1u}) & i.r. \\ v_4(f_{1u}) & i.r. \\ v_5(f_{2g}) & Ra \\ v_6(f_{2u}) & - \end{array}$	$525\pm1 (0.003)$ $438\pm2 (0.75)$ 598 ± 2 not observed $332\pm2 (0.75)$ not active	$505\pm1 (0.003)$ $420\pm2 (0.75)$ 564 ± 3 not observed $302\pm2 (0.75)$ not active

Note: in brackets the depolarization ratio is given. Data taken from W. W. Rudolph, and S. Schönherr, Z. Phys. Chem. (Leipzig) **270** (1989) 1121.

electron configuration of these ions also consists of a noble gas core, with a buried 4f shell. The majority of crystal structures give hexa-coordination for Sc(III), illustrating its similarity to Al(III) but higher coordination numbers are also reported. Other similarities to Al(III) include the formation of ScO(OH) with the same structure as the Al analog, the oxide is about as basic as Al_2O_3 , it is more easily hydrolyzed than the lanthanides, a cryolite phase exists in NaF-ScF₃ (Na₃ScF₆ as well as NaScF₄), ScCl₃ is readily hydrolyzed by water and sublimes at much lower temperature than lanthanide chlorides, associated with the different solid-structure (isomorphious with FeCl₃) [30].

In nature, the lithophilic Sc occurs always as a 3-valent cation and it is concentrated only in oxygen compounds like silicates, titano- tantalo-niobates and phosphates and especially its disperse occurrence in different minerals is characteristic. In naturally occurring compounds Sc(III) shows diadochy with other elements especially Fe(II) and Fe(III) and its coordination number is mostly 6. About its history and cosmochemistry compare also [45].

4. Further comments concerning the stability of $[Sc(OH_2)_6^{3+}]$

In order to learn something about the stability of $[Sc(OH_2)_6^{3^+}]$ *ab initio* molecular orbital calculations were carried out and will be presented very soon (W. W. Rudolph and C. C. Pye, J. Phys. Chem., in preparation). The computer results verify, firstly, the stability of the hexaaqua complex and its symmetry could be determined to be T_h . Secondly, the *ab initio* data reveal that the reaction $[Sc(OH_2)_7^{3^+}] \rightleftharpoons [Sc(OH_2)_6OH_2^{3^+}]$ is favoured strongly to the right site; or with other words the quantum chemical computation

favoures the hexaaqua Sc(III) with one outer-sphere water. Furthermore, *ab initio* wavenumber calculations of the $[Sc(OH_2)_6(OH_2)_{12}^{3+}]$, the Sc(III) hexaaqua complex with 12 outer-sphere water molecules, reproduces our wavenumbers for the hexaaqua complex well.

5. Conclusions

It could be shown conclusively that Sc(III) in aqueous solution (in opposite to complexation of the anions as in sulfate and chloride solution) occurs as hexaaqua complex ion. The weak, polarized Raman band assigned to the $v_1(a_{1g})ScO_6$ mode of the hexaaqua-Sc(III) ion (T_h symmetry for the whole complex ion or O_h symmetry for the ScO₆ unit) has been studied. The isotropic scattering geometry in R-format was employed in order to measure the true vibrational contribution of the band and account for the Boltzmann temperature factor B. The dependence on concentration has also been measured. The 442 cm⁻¹ band of hexaaqua-Sc(III) shifts only 3 cm⁻¹ to lower wavenumbers and broadens about 20 cm⁻¹ for a 60 °C temperature increase. The Raman spectroscopic data suggest that the hexaaqua Sc(III) ion is stable in perchlorate solution over the temperature range measured. These findings are in contrast to $Sc_2(SO_4)_3$ solutions, where sulfate replaces a water molecule of the first hydration sphere.

Besides the polarized component at 442 cm⁻¹, two weak depolarized modes at 295 cm⁻¹ and 410 cm⁻¹ were measured in the Raman effect. These two modes of the ScO₆ unit of the hexaaqua ion were assigned to $v_2(e_g)$ and $v_5(f_{2g})$ respectively. The infrared active mode $v_3(f_{1u})$ was measured to be at 460 cm⁻¹ (taken from D. M. Adams, Metal-Ligand vibrations and related vibrations, E. Arnold, London 1967).

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