Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Material

Wolfram W. Rudolph and Gert Irmer: A Raman spectroscopic investigation of speciation in $La_2(SO_4)_3$(aq).

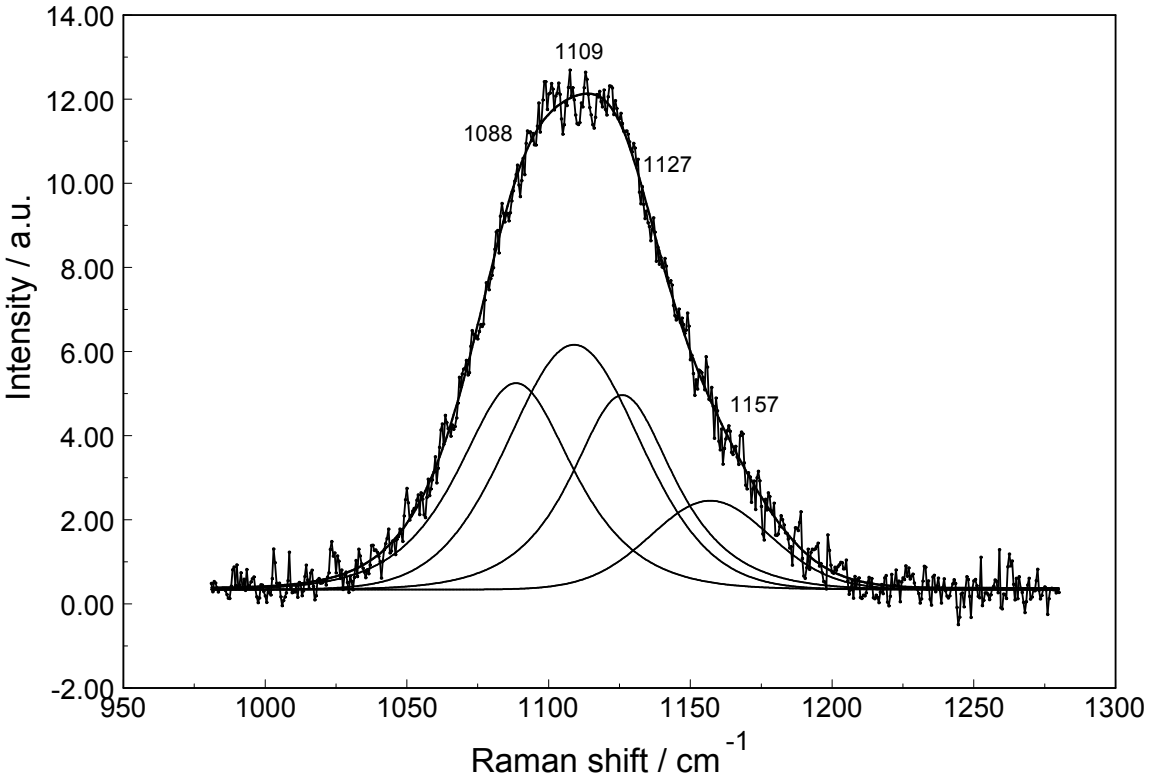

Figure S1. Anisotropic Raman spectrum of the ν_3 SO_4^{2-} band profile of an aqueous 0.0376 $molL^{-1}$ $La_2(SO_4)_3$. The measured anisotropic band contour, the sum curve and the band components of the band fit are shown. In addition the peak positions of the band components are given.

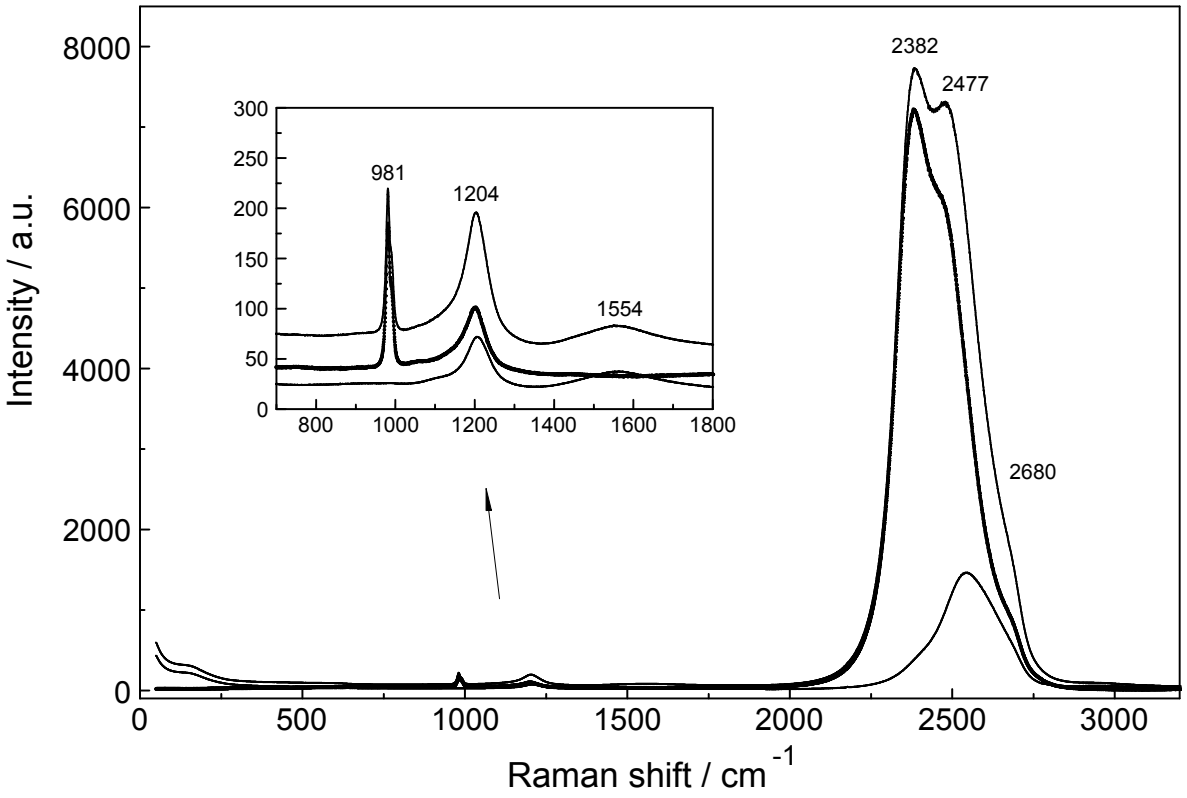

Figure S2. Overview Raman spectrum of a $La_2(SO_4)_3$ solution in heavy water from 50 – 3200 cm^{-1}. The solvent spectrum, the spectrum of D_2O dominates and the D_2O(l) bands are assigned to the restricted translation band at 168 cm^{-1}, the librational bands between 300 and 900 cm^{-1}, the deformation mode ν_2(DOD) at 1204 cm^{-1} (note the Raman non-coincidence effect of the band) and the O-D stretching profile with the double band at 2382 and 2477 cm^{-1} as well as the shoulder at 2680 cm^{-1}. The inset shows the wavenumber range from 700 – 1800 cm^{-1} in greater detail. The band profile of $\nu_1SO_4^{2-}$ shows two band components at 981 cm^{-1} assigned to the "free", uncoordinated sulfate and at 991 cm^{-1} for "bound" sulfate. The bands at 1204 cm^{-1} and 1550 cm^{-1} are due to the solvent D_2O. The band at 1204 cm^{-1} represents the deformation mode, ν_2(DOD) and the band at 1554 cm^{-1} a combination band of ν_2(DOD) with a librational mode, $\nu_2 + \nu_L$.

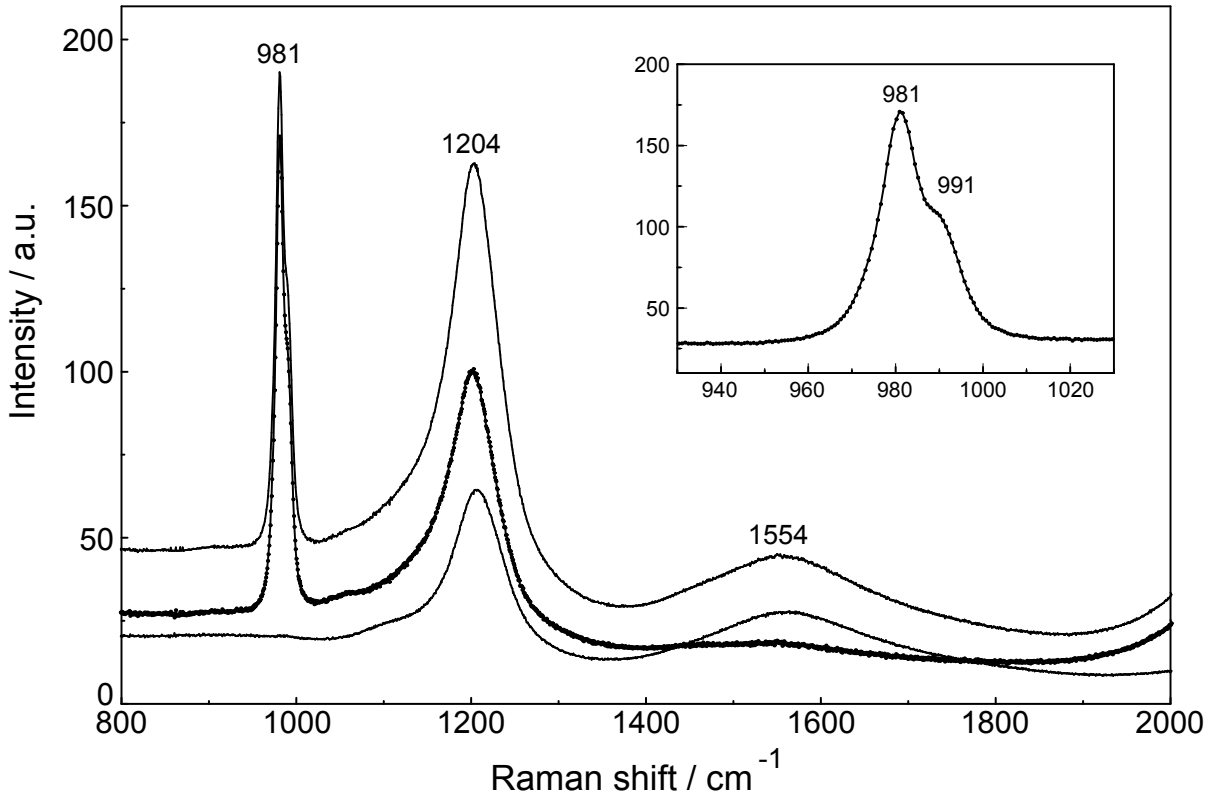

Figure S3. Raman spectrum of a $La_2(SO_4)_3$ solution in heavy water from 800 – 2000 cm^{-1}. The band profile of $\nu_1SO_4^{2-}$ shows two band components at 981 cm^{-1} assigned to the "free", uncoordinated sulfate and at 991 cm^{-1} for "bound" sulfate of the La^{3+}-sulfato-complex, $[La(OD_2)_8OSO_3]^+$. The bands at 1204 cm^{-1} and 1554 cm^{-1} are due to the solvent D_2O (see Figure S1). The inset shows the $\nu_1SO_4^{2-}$ band profile in greater detail.

Table S1. Raman data on $La_2(SO_4)_3$ solution as a function of dilution at 23 °C. Band parameters of the two-component fit of the ν_1-SO_4^{2-} band profile for the component bands at 980 cm^{-1} and 991 cm^{-1}. The degree sulfato complex formation, alpha, is also given.

Concentration / $molL^{-1}$	980 cm^{-1} - band			991 cm^{-1} - band			alpha
	$\tilde{\nu}$ /cm^{-1}	fwhh /cm^{-1}	A_{980}	$\tilde{\nu}$ /cm^{-1}	fwhh /cm^{-1}	A_{991}	
0.0376	980.78	11.50	73005	991.0	11.6	24003	0.247
0.0189	980.70	11.49	37388	990.8	11.7	12052	0.244
0.00754	980.55	11.20	15234	990.8	11.6	4547	0.230
0.00377	980.45	11.00	7755	990.4	12.1	2154	0.217
0.00189	980.38	10.40	3920	990.3	12.1	999	0.203
0.000943	980.35	9.93	1994	990.2	12.3	422	0.175
0.000264	980.32	9.62	624	990.2	12.1	75	0.107

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Table S2. Raman data of a 0.0098 molL^{-1} $La_2(SO_4)_3$ solution as a function of temperature. The band parameter of the three component bands of the ν_1-SO_4^{2-} band profile are given.

Tempera-ture /°C	Band component 1			Band component 2			Band component 3		
	$\tilde{\nu}$ /cm^{-1}	fwhh /cm^{-1}	Integrated band intensity	$\tilde{\nu}$ /cm^{-1}	Fwhh /cm^{-1}	Integrated band intensity	$\tilde{\nu}$/cm^{-1}	Fwhh /cm^{-1}	Integrated band intensity
23	980.0	9.45	930	983.1	8,9	357	991.2	10.0	319
24	979.6	9.45	920	982.8	9.0	352	991.0	10.0	321
50	978.3	12.0	910	980.7	9.0	204	989.8	10.2	391
75	977.1	12.4	778.5	979.3	9.2	171	988.6	11.2	469.5
98	974.4	13.4	626.7	978.6	9.1	134	987.5	12.4	557