Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Material

Table S1. Simulation results of $[Y(H_2O)_8]^{3+}$ clusters in the gas phase and similar clusters with a polarizable continuum (PC): Symmetry of the clusters, number of negative frequencies, geometrical parameters of the clusters, the electronic energies calculated. The data for the ν_1 Y-O breathing mode is also given for these DFT clusters.

Level of theory / basis set	symmetry	negative frequencies	ν_1/ cm^{-1} *	Y-O / Å	O-H / Å	H-O-H / °	energy in hartree
gas phase cluster							
B3LYP/LANL2DZ	C2	none	336.6	2.399	0.981	109.6	-648.698328
B3LYP/LANL2DZ	**S8**	**none**	**336.5**	**2.399**	**0.981**	**109.6**	**-648.698322**
B3LYP/LANL2DZ	D4	1	(334.2)	2.409	0.981	109.1	-648.688320
B3LYP/LANL2DZ/6-31G	C2	none	338.3	2.396	0.979	109.6	-648.511648
B3LYP/LANL2DZ/6-31G(d)	C2	none	328.4	2.408	0.977	106.0	-648.591925
B3LYP/LANL2DZ/6-1G+(d,p)	C2	none	338.3	2.396	0.978	109.6	-648.511648
B3LYP/LANL2DZ/D95+*	C2	none	334.0	2.414	0.978	105.9	-648.799550
B3LYP/LANL2DZ/D95**	C2	none	324.7	2.413	0.975	105.9	-648.848420
B3LYP/LANL2DZ/D95+**	C2	none	331.8	2.416	0.975	105.7	-648.864907
Cluster with PCM							
B3LYP/LANL2DZ	**S8**	**none**	**372.1**	**2.354**	**0.989**	**110.9**	**-649.355492**
B3LYP/LANL2DZ/6-31G+(d,p)	C2	-	no result	-	-	-	-
B3LYP/LANL2DZ/6-31G	C2	-	no result	-	-	-	-

- Remark: For the $[Y(H_2O)_8]^{3+}$ cluster with its 25 atoms 3 x 25 – 6 = 69 normal modes are expected with the irreducible representation of the normal modes: $\Gamma_v(S_8) = 8a(Ra) + 9b(i.r.) + 18e_1(i.r.) + 18e_2(Ra) + 16\ e_3(Ra)$. The mode ν_1 is the totally symmetric Y-O mode, the so called breathing mode.

Table S2. Simulation results of a $[Y(H_2O)_6]^{3+}$ gas phase cluster and a similar clusters with a polarizable continuum (PCM). The symmetry of the cluster is T_h in both states. Given are frequency for the ν_1Y-O breathing, the geometrical parameters of the cluster and the calculated electronic energy.

Level of theory / basis set	ν_1/ cm^{-1} *	Y-O /Å	O-H /Å	H-O-H /°	Energy in hartree
B3LYP/LANL2DZ	376.5	2.322	0.986	107.8	-495.741633
B3LYP/LANL2DZ + PCM	407.5	2.285	0.986	109.4	-496.332300

- The mode ν_1 is the totally symmetric mode of Y-O (breathing mode).

Table S3: DFT frequencies at the B3LYP/ LANL2DZ level of theory for $[Y(H_2O)_8]^{3+}$ with a solvation shell (PC model). The irreducible representation of vibrations leads to $\Gamma_v(S_8)$ = 8a (Ra) + 9b (i.r.) + 18e_1 (Ra, i.r.) + 18e_2 (Ra) + 16e_3 (Ra).

peak position cm^{-1}	sym-metry	assignment		peak position cm^{-1}	sym-metry	assignment
27.1	**e_2**	**δ YO_8**		425.8	e_1	ω H_2O
101.1	**b**	**δ YO_8**		523.0	b	ρ H_2O
109.3	**e_1**	**δ YO_8**		538.6	a	ρ H_2O
136.4	**b**	**δ YO_8**		566.0	e_1	ρ H_2O
141.1	**a**	**δ YO_8**		566.2	e_3	ρ H_2O
154.8	**e_1**	**δ YO_8**		594.7	e_2	ρ H_2O
154.9	**e_3**	**δ YO_8**		1570.3	e_2	δ H_2O
163.0	**e_2**	**δ YO_8**		1575.3	e_3	δ H_2O
215.5	e_2	τ H_2O		1580.0	e_1	δ H_2O
250.0	e_1	τ H_2O		1581.2	b	δ H_2O
278.8	e_3	τ H_2O		1589.6	a	δ H_2O
283.6	**e_2**	**ν YO_8**		3453.4	e_2	ν_s H_2O
301.3	**e_3**	**ν YO_8, τ H_2O**		3454.0	e_3	ν_s H_2O
314.7	a	τH_2O		3456.9	b	ν_s H_2O
336.7	**b**	**ν YO_8,** ω H_2O		3459.6	e_1	ν_s H_2O
348.5	**e_1**	**ν YO_8,** ω H_2O		3476.5	a	ν_s H_2O
367.0	b	τH_2O, ω H_2O		3548.1	a	ν_{as} H_2O
372.1	**a**	**ν_s YO_8**		3548.3	e_1	ν_{as} H_2O
375.7	e_3	ω H_2O		3548.3	e_3	ν_{as} H_2O
376.4	a	ω H_2O		3548.3	e_2	ν_{as} H_2O
384.8	b	ω H_2O		3548.5	b	ν_{as} H_2O
397.6	e_2	ω H_2O				

Note, that the skeletal vibrations are written in bold type letters, with the breathing vibrational frequency of the cluster at 372.1cm^{-1}. Notations: ν_{as}: antisymmetric stretch, ν_s: symmetric stretch, δ: deformation; H_2O librations: ρ: rocking, ω: wagging, τ: twisting

Table S4. Our Raman data and band assignments of $CF_3SO_3^-$(aq) at 23 °C.

Raman					assignment
peak position/cm^{-1}	A_i	fwhh /cm^{-1}	depol. degree	symmetry	
-	-	-	-	a_2	torsion
212	0.97	18.1	0.65	e	τ_3FC- SO_3
319	40.81	12.85	0.25	a_1	ν C-S
351	21.30	14.7	0.70	e	τ_3FC- SO_3
518.8	1.97	16.1	0.64	e	δ_s FCF + δ_s SO_3
577.9	14.61	17.7	0.74	e	δ_{as} FCF, δ_{as} OSO
640.5	0.78	25.9	0.240	a_1	δ_{as} CF_3, δ_{as} OSO
764.5	48.05	8.45	0.0023	a_1	$\delta_s CF_3$, $\delta_s SO_3$
1033.3	100	12.9	0.0097	a_1	$\nu_s SO_3$, $\nu_s CF_3$
1182	2.33	27.8	0.71	e	$\nu_{as} CF_3$
1227.5	4.54	9.8	0.21	a_1	$\nu_s CF_3$
1254.5 * 1281.8	2.38 15.79	46 33	0.63 0.70	e	$\nu_{as} SO_3$

- This band appears as a double band; data from band fit procedure

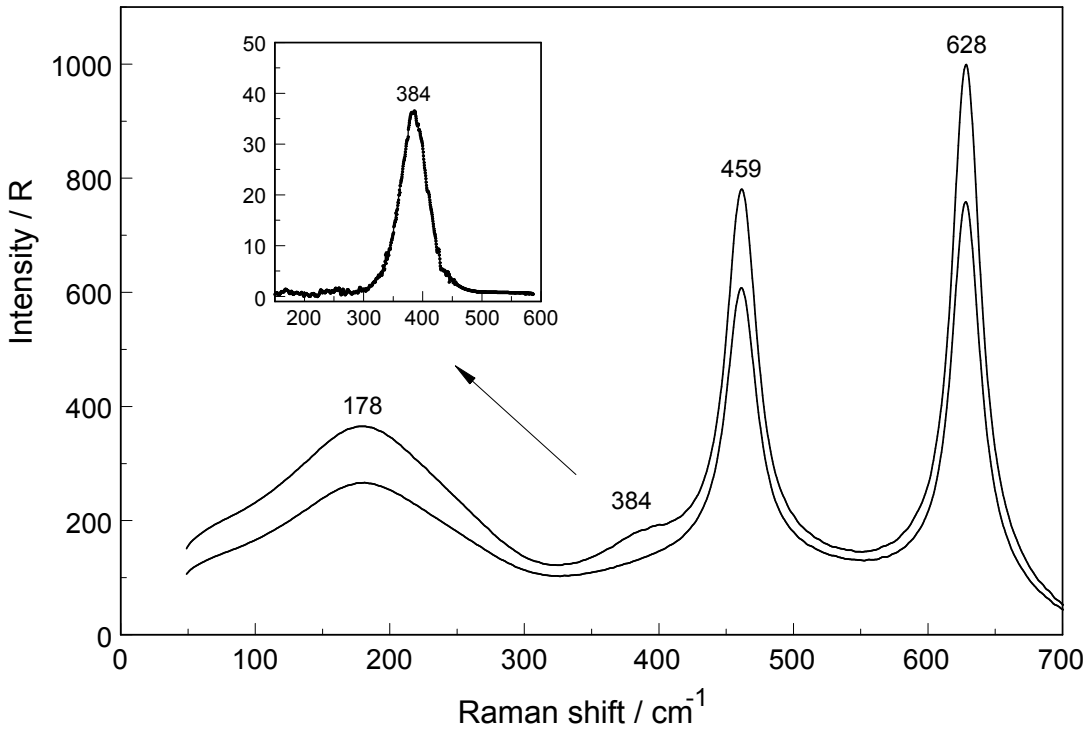

Figure S1. Polarized and depolarized Raman scattering profiles of 0.256 mol·L^{-1} $Y(ClO_4)_3$(aq) (R_w = 211). A. The inset shows the isotropic profile of the YO_8 breathing mode at 384 cm^{-1} (R_{iso} = R_{VV} - 4/3R_{VH}).

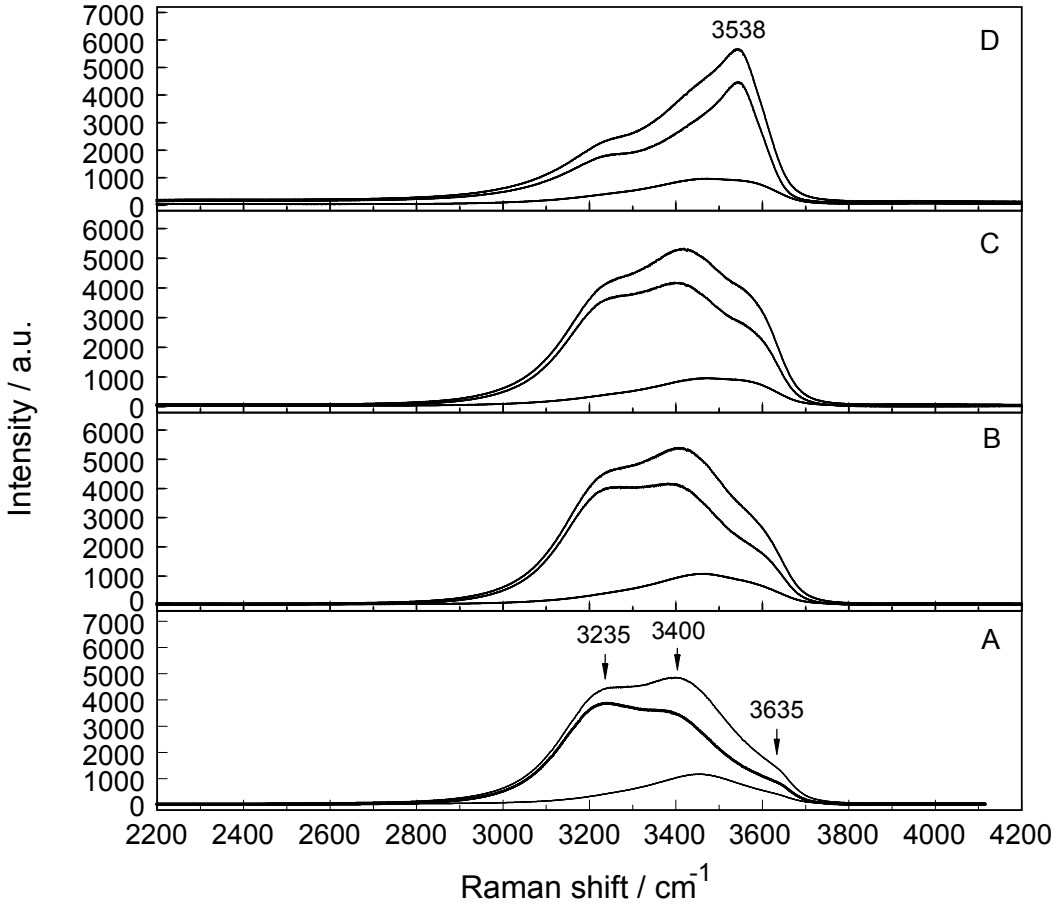

Figure S2. The O-H stretching region of water from 2200 – 4200 cm^{-1} for three aqueous $Y(ClO_4)_3$ solutions in comparison with neat liquid water. From bottom to top: (A) H_2O, (B) 0.390, (C) 0.76 and (D) 1.770 $molL^{-1}$ $Y(ClO_4)_3$. At the bottom (A) the O-H profile of water with its characteristic bands is shown and above (B-D) the profiles of $Y(ClO_4)_3$(aq). With increasing solute concentration a mode at 3538 cm^{-1} is dominating the O-H profiles. (D) The band component of water at 3235 cm^{-1} is still observable while the component at 3405 cm^{-1} is completely overlapped by the strong band, ν O-H···· ClO_4^-, at 3538 cm^{-1} of weakly H-bonded water.

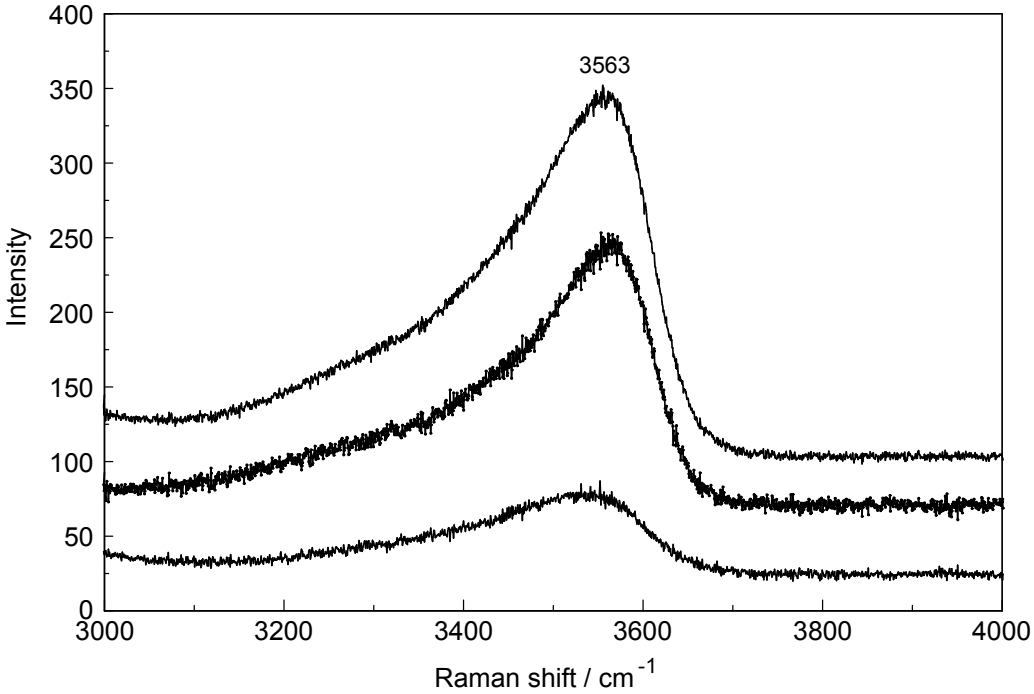

Figure S3. The O-H stretching region (HDO/D_2O; ca. 3% HDO) of a 2.300 mol L^{-1} $Y(ClO_4)_3$ solution in D_2O from 3000 – 4000 cm^{-1}. The dominating O-H band at 3563 cm^{-1} is due to the decoupled O-H oscillators, HDO/D_2O, weakly H-bonded to ClO_4^-. In a concentrated $Y(ClO_4)_3$ solution the O-H$\cdots$$ClO_4^-$ band appears at 3538 cm^{-1} (Figure S2).

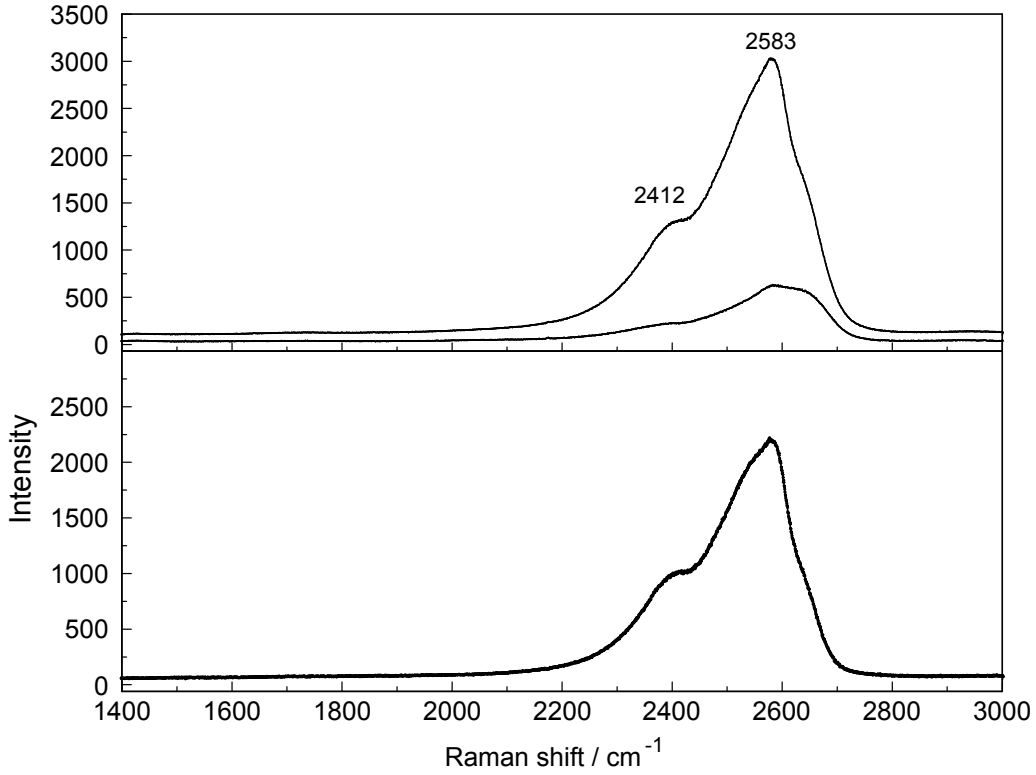

Figure S4. The O-D stretching region of heavy water from 1400 – 3000 cm^{-1} of a 2.300 mol L^{-1} $Y(ClO_4)_3$ solution in D_2O. The dominating O-D band at 2583 cm^{-1} is due to the O-D oscillators weakly D-bonded to ClO_4^-. Only one band component of the heavy water at 2412 cm^{-1} appears while the component which normally appears at 2500 cm^{-1} is almost completely overlapped by the strong band at 2583 cm^{-1}.

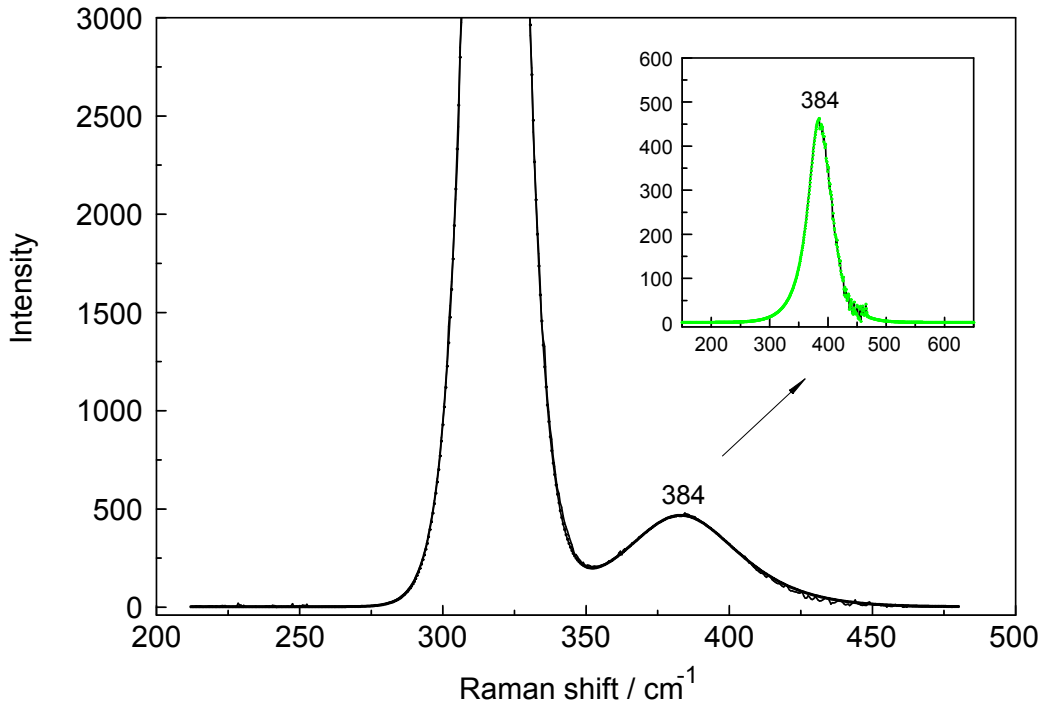

Figure S5. The isotropic Raman spectrum of a 1.10 molL^{-1} $Y(CF_3SO_3)_3$ solution in the wavenumber range from 212 – 460 cm^{-1} and the sum curve of the fit. The inset shows the result of the difference spectrum of the $Y(CF_3SO_3)_3$ spectrum from which the spectrum of $CF_3SO_3^-$(aq) has been subtracted. The band at 384 cm^{-1} is assigned to the YO_8 breathing mode.

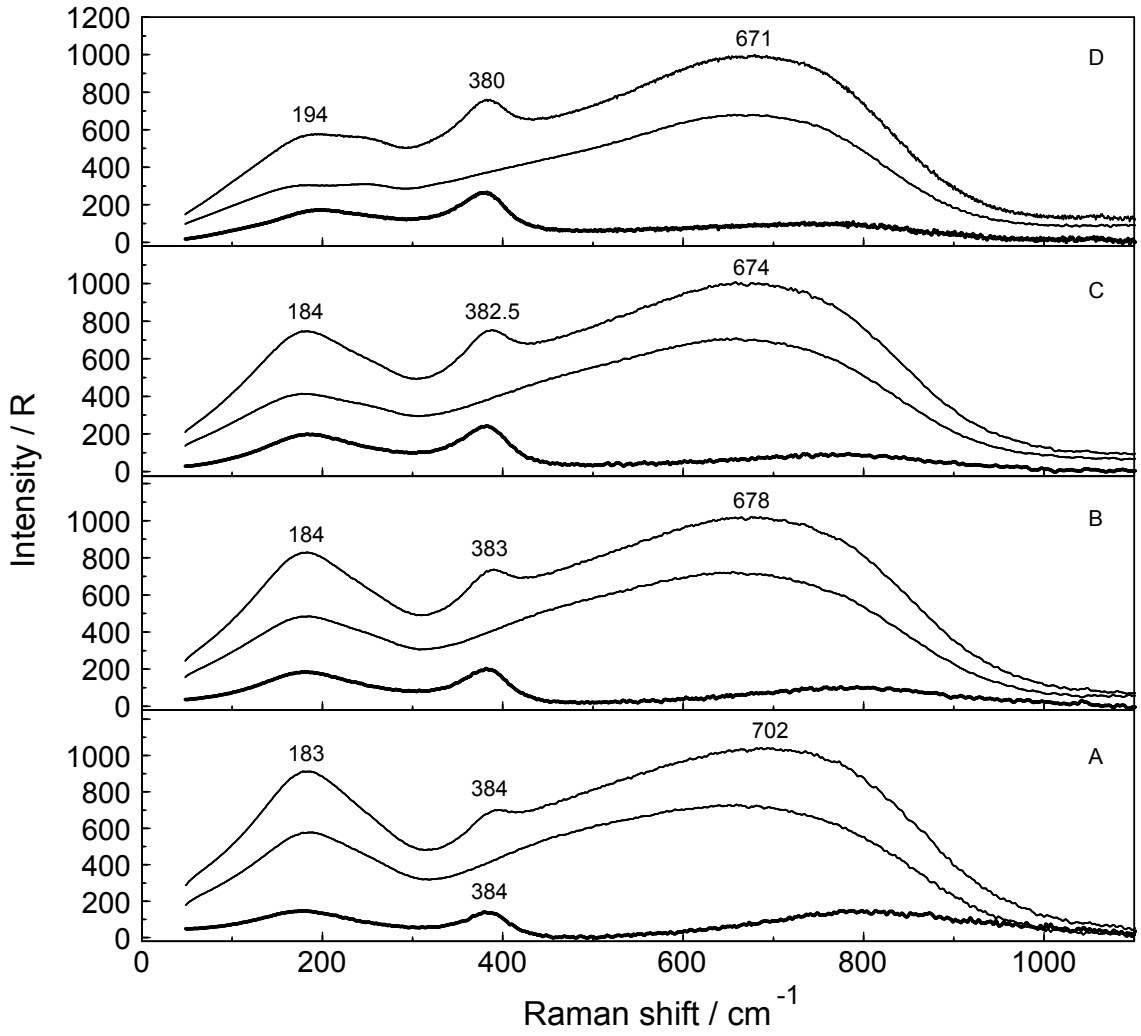

Figure S6. Raman scattering profiles (polarized, depolarized and isotropic (darker line) scattering orientations) of four YCl_3 solutions. From bottom to top: (A) 0.479 molL^{-1}; (B) 0.803 mol·L^{-1}; (C) 1.01 molL^{-1} and (D) 2.378 molL^{-1}. The bands of the solute water are the restricted translation and the librational bands at 183-194 cm^{-1} and 703 – 671 cm^{-1}.

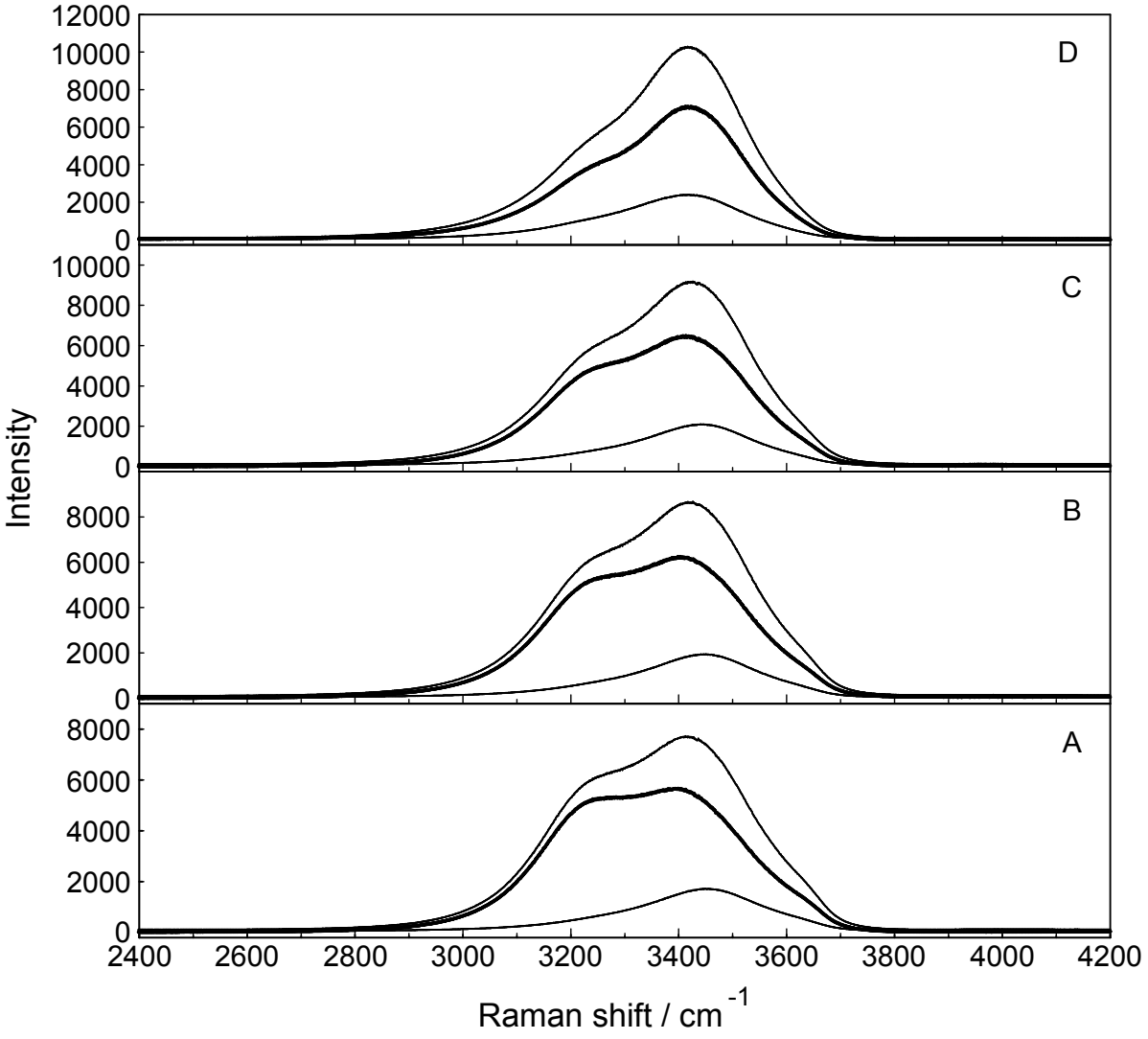

Figure S7. Raman scattering profiles (polarized, depolarized and isotropic (darker line) scattering orientations) of four YCl_3 solutions. From bottom to top: (A) 0.479 $molL^{-1}$; (B) 0.803 $mol \cdot L^{-1}$; (C) 1.01 $molL^{-1}$ and (D) 2.378 $molL^{-1}$. Shown are the two water band components of the O-H stretching profile. The component bands for the O-H stretching profile of neat water are 3225 and 3405 cm^{-1} and a shoulder at 3630 cm^{-1}. The peak positions shift slightly to higher wavenumbers and for the 2.378 $molL^{-1}YCl_3$ solution the band positions peak at 3220 cm^{-1}, 3425 cm^{-1} and a small shoulder at 3595-3625 cm^{-1}.

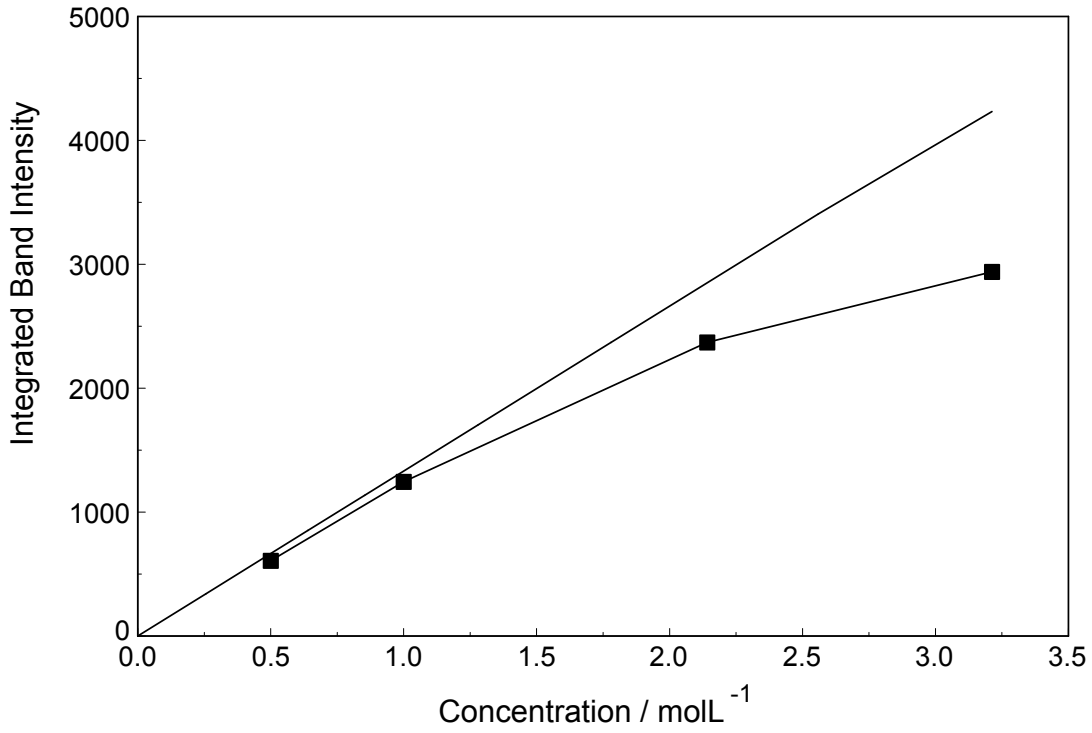

Figure S8. Quantitative Raman results: Integrated band intensities of the ν_1YO_8 band versus stroichiometric concentration of four YCl_3 solutions (black squares) and the curve of the band intensity of ν_1YO_8 as a function of concentration in $Y(ClO_4)_3$(aq).

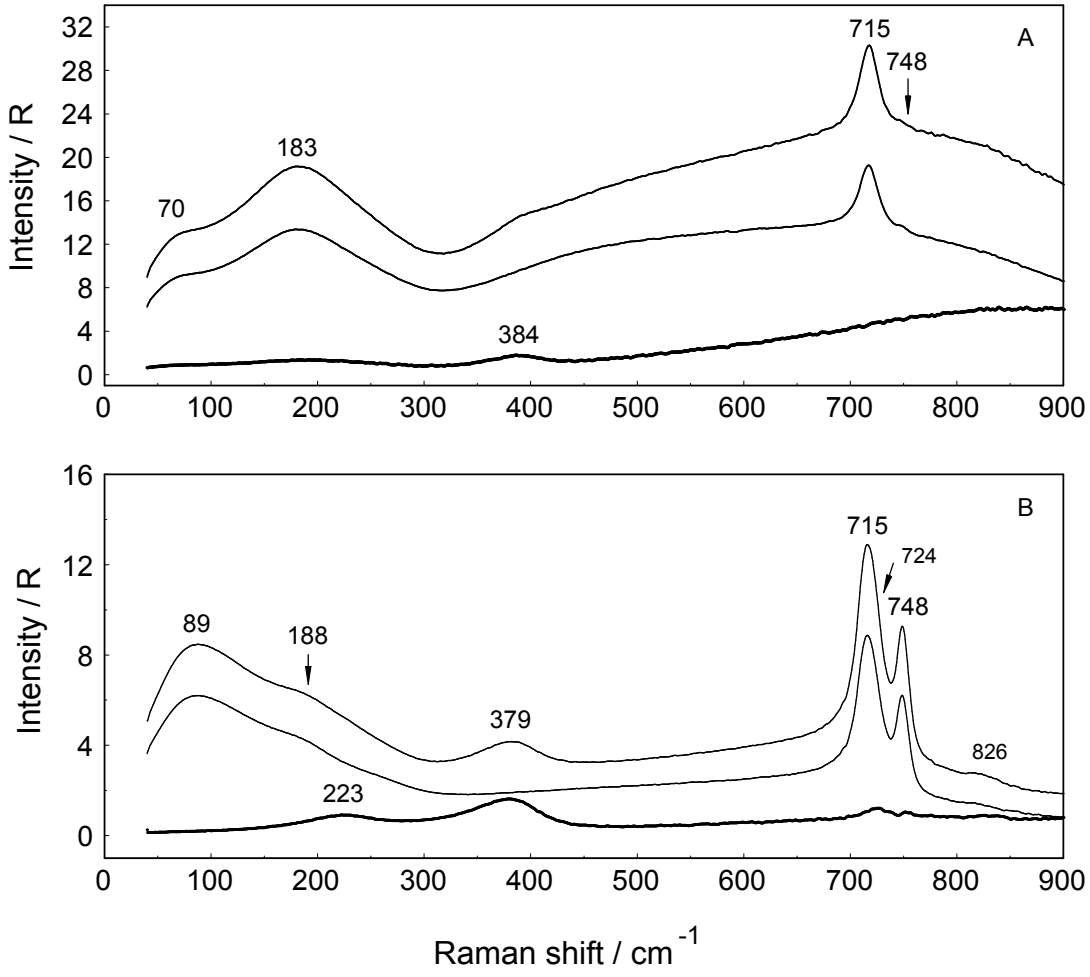

Figure S9. Raman spectra (R- format, all three scattering contributions): (A) a dilute solution at 0.198 mol·L^{-1} $Y(NO_3)_3$ and (B) a concentrated solution at 2.035 mol·L^{-1} in the frequency range from 40 - 900 cm^{-1}. Note the very weak band at 826 cm^{-1} in panel (B) which is due to the normally infrared active mode, $\nu_2(a_2'')$.

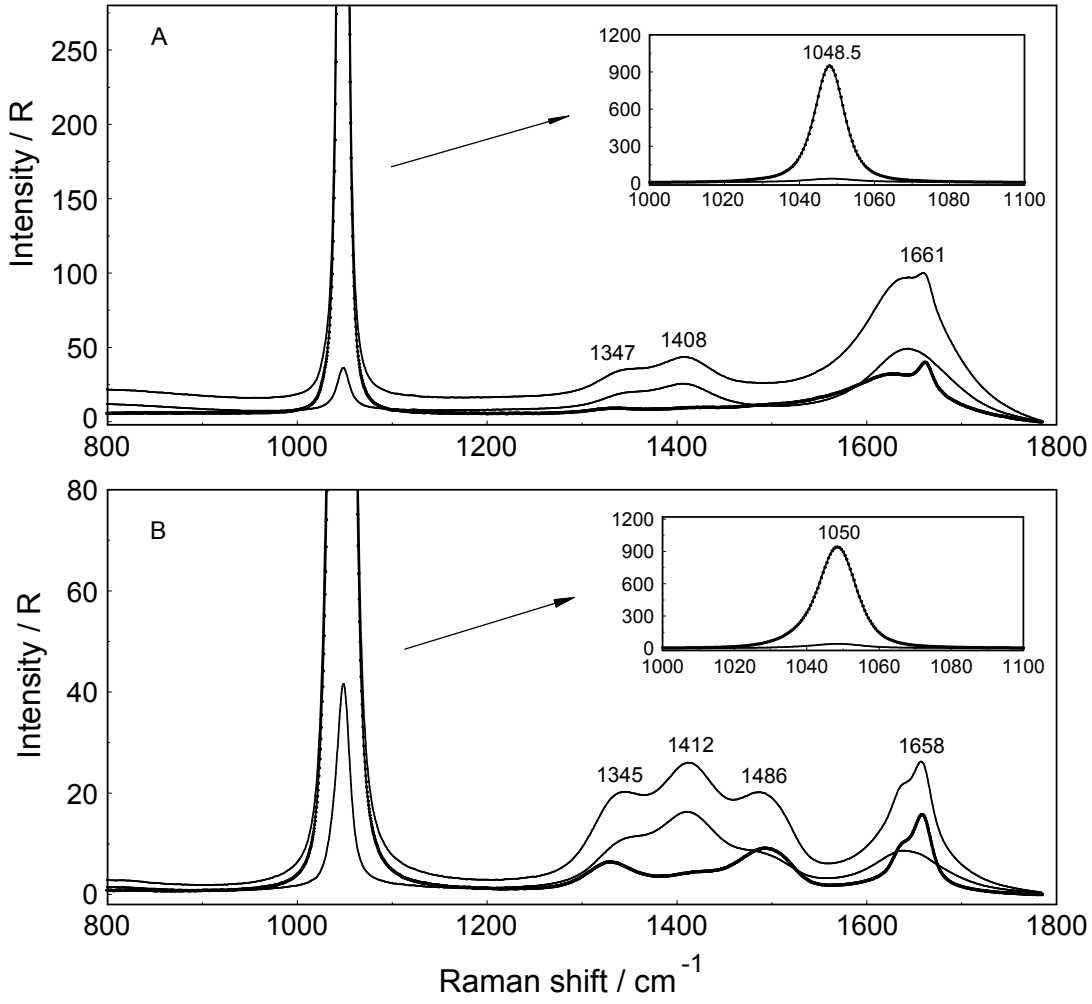

Figure S10. Raman spectra (R- format, all three scattering contributions) of A) dilute $Y(NO_3)_3$ solution at 0.198 mol·L^{-1} and B) of a 2.035 mol·L^{-1} solution at from 800 – 1800 cm^{-1}. The insets show the symmetric N-O stretching band in more detail (isotropic scattering and anisotropic scattering).