The Hydration of the Scandium(III) Ion in Aqueous Solution and Crystalline Hydrates Studied by XAFS Spectroscopy, Large Angle X-Ray Scattering and Crystallography

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Supplementary Material

Fig. S1. The fit and the individual contribution of the different scattering paths of the EXAFS data of

a/ solid octaaquascandium(III) trifluoromethanesulfonate (**S1**), solid line - experimental data, dashed line - calculated model function using the parameters given in Table 3. Separate contributions: (offset -7) - Sc-O_p single scattering (SS) and (offset -16) - Sc-O_c SS.

b/ solid octaaquascandium(III) trifluoromethanesulfonate (**S1**), solid line - experimental data, dashed line - calculated model function using the parameters given in Table 3. Separate contributions: (offset -8) - Sc-O_p single scattering (SS) and (offset -16) - Sc-O_c SS.

c/ solid hexaaquascandium(III) perchlorate (**S2**), solid line - experimental data, dashed line - calculated model function using the parameters given in Table 3. Separate contributions: (offset -7) - Sc-O single scattering (SS), (offset -14) - Sc-O-O 3-leg linear MS, (offset -16) - Sc-O-O 3-leg linear MS, (offset -18) - Sc-O-Sc-O 4 leg linear MS and (offset -20) - Sc-O-Sc-O 4-leg linear MS.

d/ solid hexaaquascandium(III) hexakis(methanesulfonato)scandate(III) (**S3**), solid line - experimental data, dashed line - calculated model function using the parameters given in Table 3. Separate contributions: (offset -8) - Sc-O single scattering (SS), (offset –16) - Sc--S single scattering (SS), (offset – 22) Sc-O-S 3-leg multiple scattering (MS), (offset -26) - Sc-O-O 3-leg linear MS, (offset -33) - Sc-O-O 3-leg linear MS, (offset -38) - Sc-O-Sc-O 4-leg linear MS and (offset -43) - Sc-O-Sc-O 4-leg linear MS.

e/ solid tetraaquabis(tosilato)scandium(III) tosilate dihydrate (**S4**), solid line - experimental data, dashed line - calculated model function using the parameters given in Table 3. Separate contributions: (offset -6) - Sc-O single scattering (SS), (offset – 17) - Sc--S single scattering (SS), (offset – 22) Sc-O-S 3-leg multiple scattering (MS), (offset – 26) Sc-O-O 3-leg multiple scattering (MS), (offset -29) - Sc-O-O 3-leg linear MS, (offset -32) - Sc-O-Sc-O 4-leg linear MS and (offset -35) - Sc-O-Sc-O 4-leg linear MS.

f/ solid $[Sc_2(\mu\text{-}OH)_2(OH_2)_5]_2Cl_4{\cdot}2H_2O$, solid line - experimental data, dashed line - calculated model function using the parameters given in Table 2. Separate contributions: (offset -7) - Sc-O single scattering (SS), (offset –15) - Sc-O-O 3-leg linear MS, (offset -17) - Sc-O-Sc-O 4-leg linear MS and (offset -19) - Sc-O-Sc-O 4-leg linear MS.

g/ 0.98 mol·dm^{-3} aqueous solution of scandium(III) trifluoromethanesulfonate and an excess of trifluoromethanesulfonic acid, 0.88 mol·dm^{-3}, solid line - experimental data, dashed line - calculated model function using the parameters given in Table 2. Separate contributions: (offset -6) - Sc-O_p single scattering (SS), (offset -14) - Sc-O_c SS, (offset -17) – Sc-O-O 3-leg linear MS, (offset -19) Sc-O-Sc-O 4-leg linear MS, (offset -21) - Sc-O-Sc-O 4-leg linear MS.

h/ 0.98 mol·dm^{-3} aqueous solution of scandium(III) trifluoromethanesulfonate and an excess of trifluoromethanesulfonic acid, 0.88 mol·dm^{-3}, refined by GNXAS, solid line - experimental data, dashed line - calculated model function using the parameters

given in Table 2. Separate contributions: (offset +3.5) - Sc-O_p single scattering (SS) and (offset +2) - Sc-O_c SS, (offset –1.5) residual.
i/ 0.34 mol·dm^{-3} aqueous solution of scandium(III) trifluoromethanesulfonate and an excess of trifluoromethanesulfonic acid, 0.05 mol·dm^{-3}, refined by GNXAS, solid line - experimental data, dashed line - calculated model function using the parameters given in Table 2. Separate contributions: (offset +4.5) - Sc-O_p single scattering (SS) and (offset +2.5) - Sc-O_c SS, (offset -2) residual.

Fig. S2. (a) LAXS data of an 1.05 mol·dm^{-3} scandium perchlorate solution, L6, with pH ≈ 0.8. (Top) Separate model contributions with parameters from Table 5, including the hydrated scandium ion, the hydrated perchlorate ion (dashed line) and the bulk water (doted line). (Middle) Radial distribution function, $D(r) - 4\pi r^2\rho_o$, and the sum of the calculated peak shapes: experimental (solid line); model (dashed line); difference between the experimental and the calculated function (dashed-dotted line). (Bottom) Structure-dependent LAXS intensity functions multiplied by the scattering variable: $s \cdot i(s)$ versus s: experimental data (solid line); model function (dashed line).

Fig. S3. Baseline-corrected and intensity-normalized Raman spectra of the aqueous solution **L1** and the crystalline hydrates **S1**–**S3**, **S5** and **S6** recorded at room temperature. The ν_1(Sc-O) symmetric stretching vibrational band is indicated.
(a) Comparison of the Raman spectra of the acidified (~1M HCF_3SO_3) scandium(III) trifluoromethanesulfonate aqueous solution **L1** and crystalline $[Sc(OH_2)_8](CF_3SO_3)_3$ and $[Sc(OD_2)_8](CF_3SO_3)_3$ (**S1**). Note that the ν_1(Sc-O) band for the deuterated compound is shifted about 15 cm^{-1} to lower frequency.
(b) Raman spectrum of crystalline $[Sc(OH_2)_6](ClO_4)_3$ (**S2**). The ν_1(Sc-O) band at 432 cm^{-1} overlap with the deformation mode of perchlorate ion, $\nu_2(ClO_4^-)$, at 462 cm^{-1}.
(c) Raman spectrum of crystalline $[Sc(OH_2)_6][Sc(OSO_2CH_3)_6]$ (**S3**). The bands at 433 and 472 cm^{-1} are the symmetric stretching modes, ν_1(Sc-O), of the cation $[Sc(OH_2)_6]^{3+}$ and anion $[Sc(OSO_2CH_3)_6]^{3-}$ entities.
(d) Raman spectrum of crystalline $[Sc_2(\mu\text{-}OH)_2(OH_2)_{10}]Br_4\cdot 2H_2O$ (**S5**).
(e) Raman spectrum of crystalline $[Sc_2(\mu\text{-}OH)_2(OH_2)_{10}]Cl_4\cdot 2H_2O$ (**S6**).

Fig. S1a.

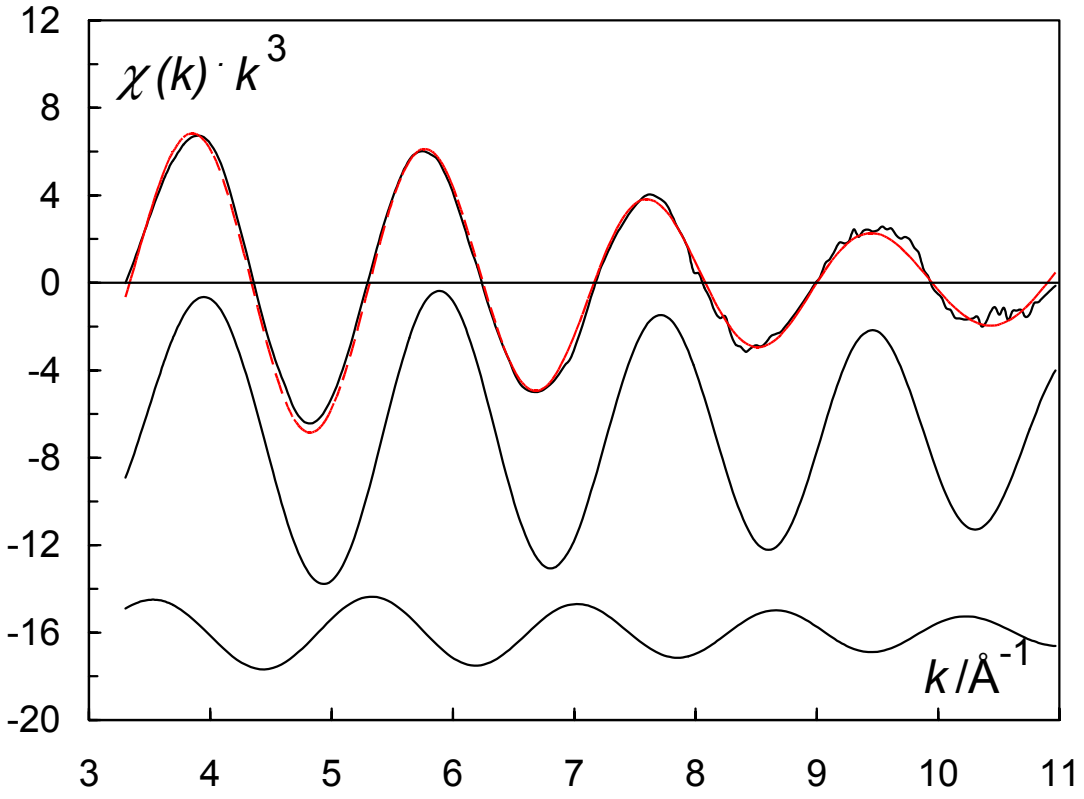


Fig. S1b.

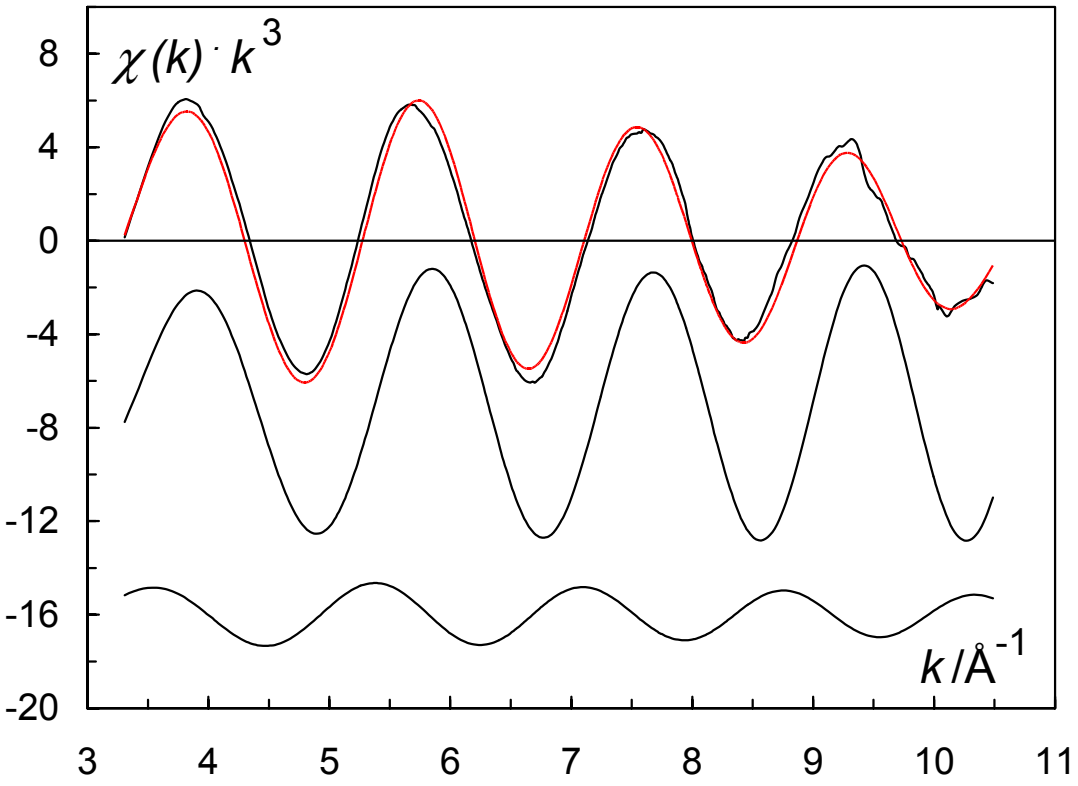


Fig. S1c.

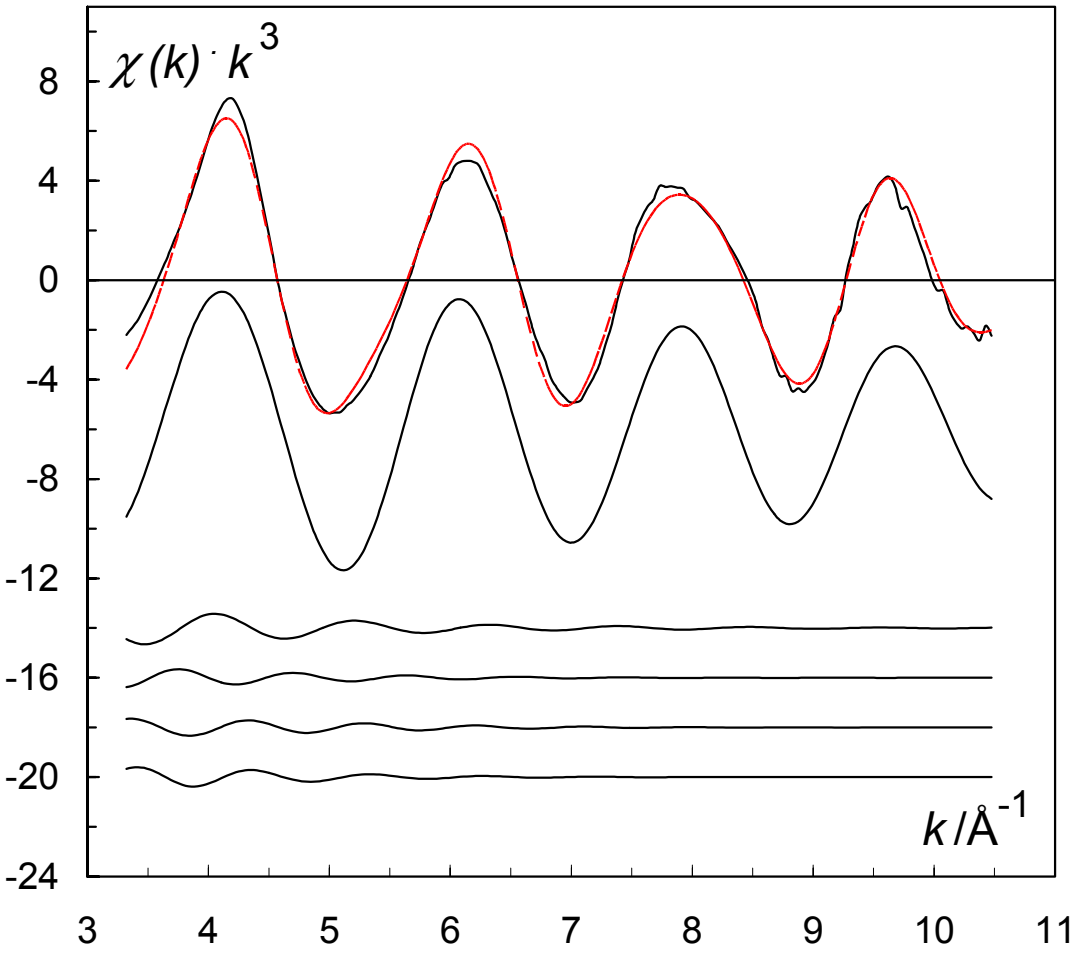
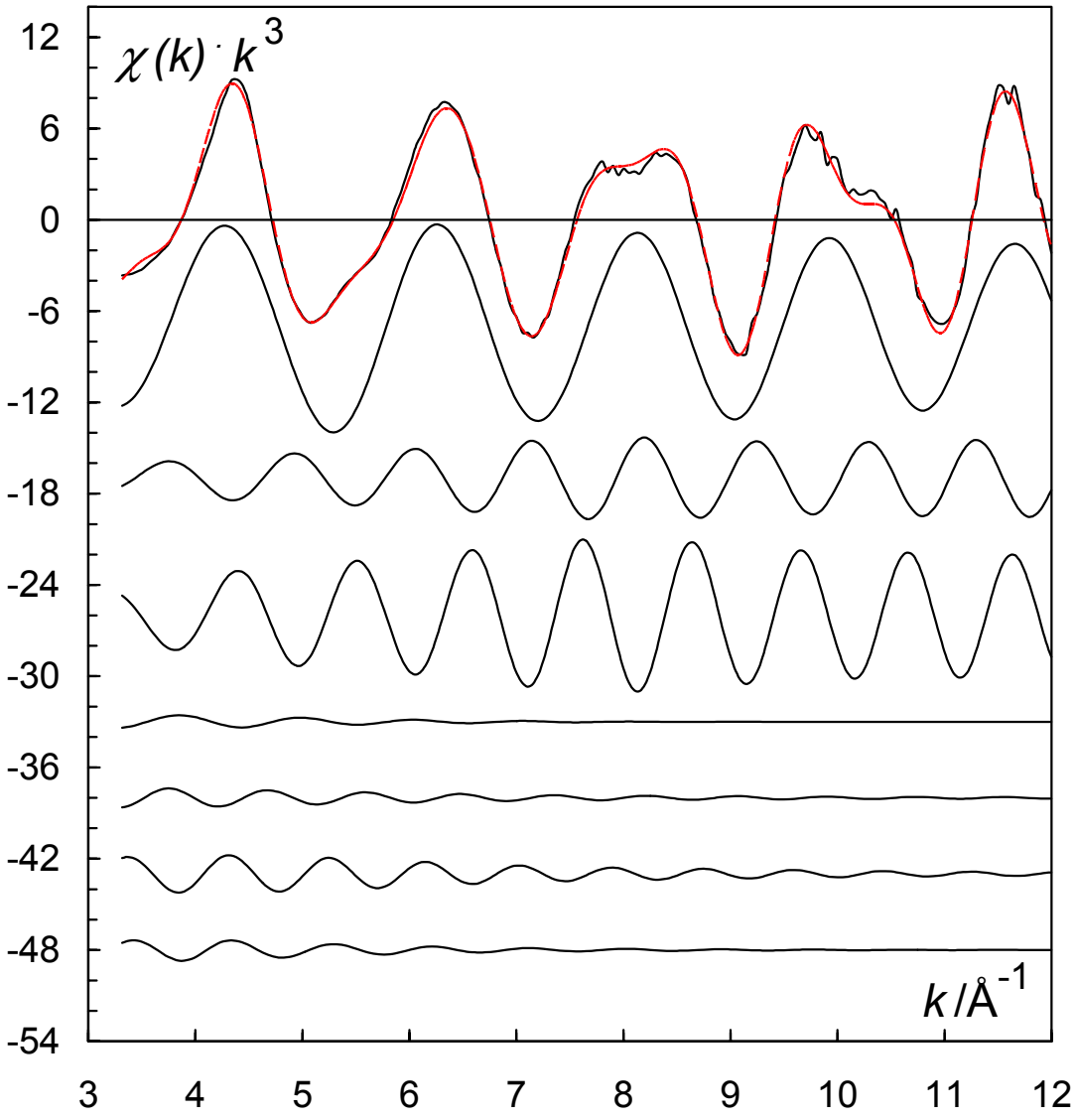


Fig. S1d.



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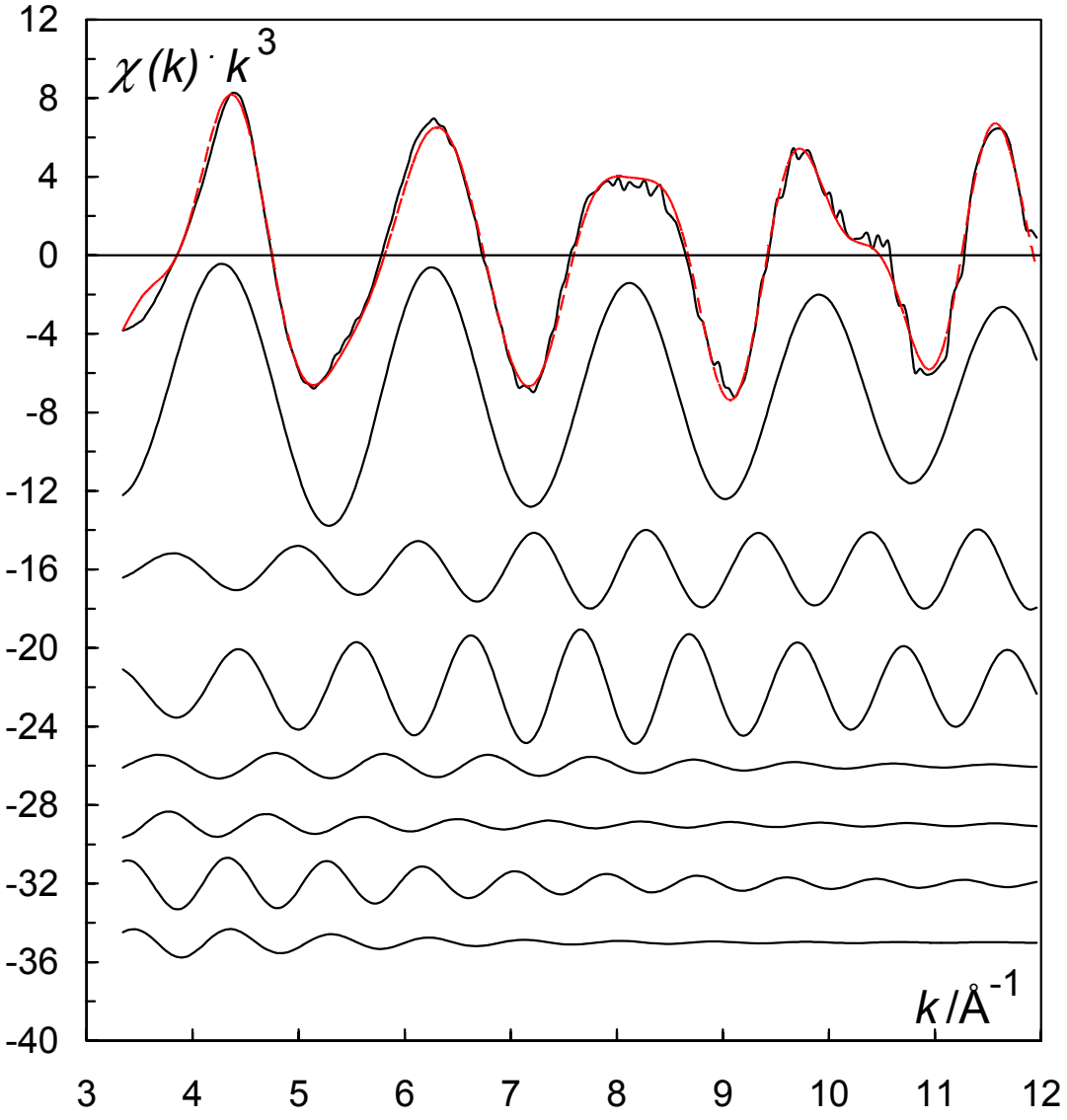
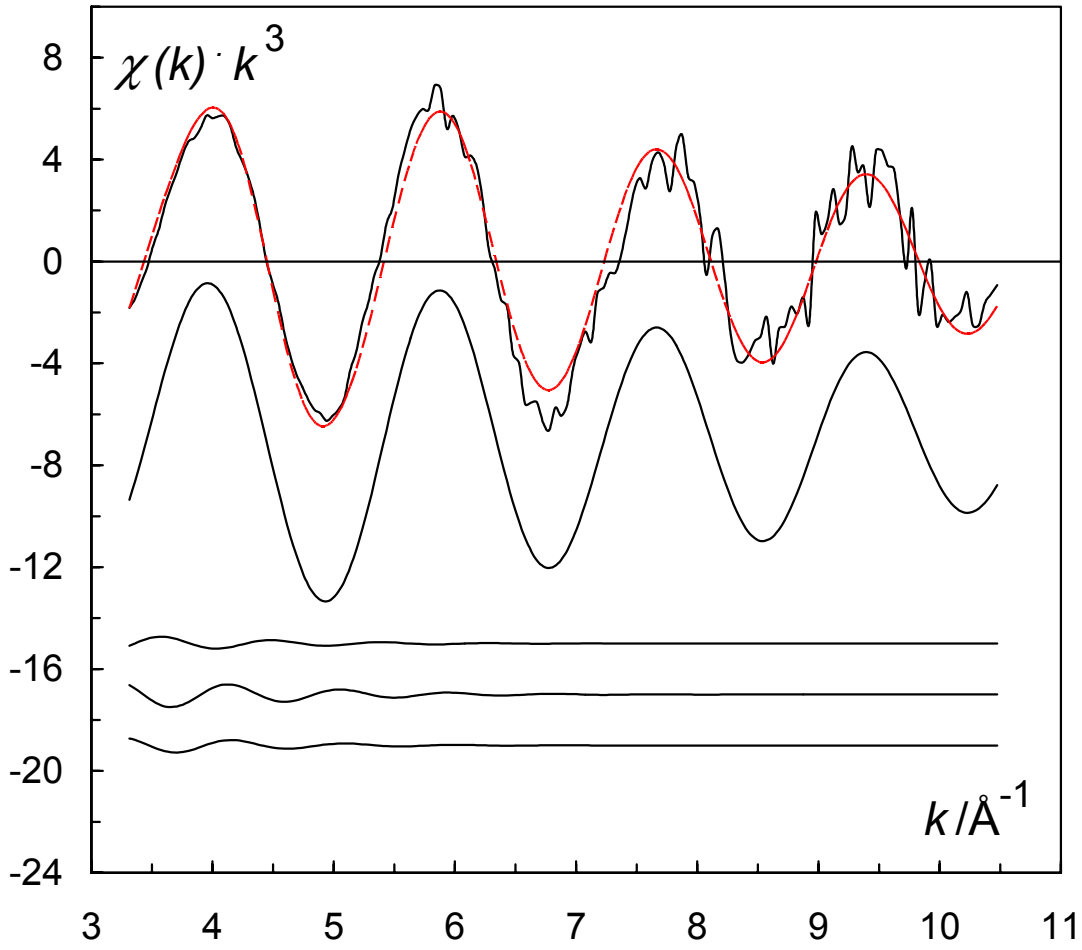


Fig. S1f.



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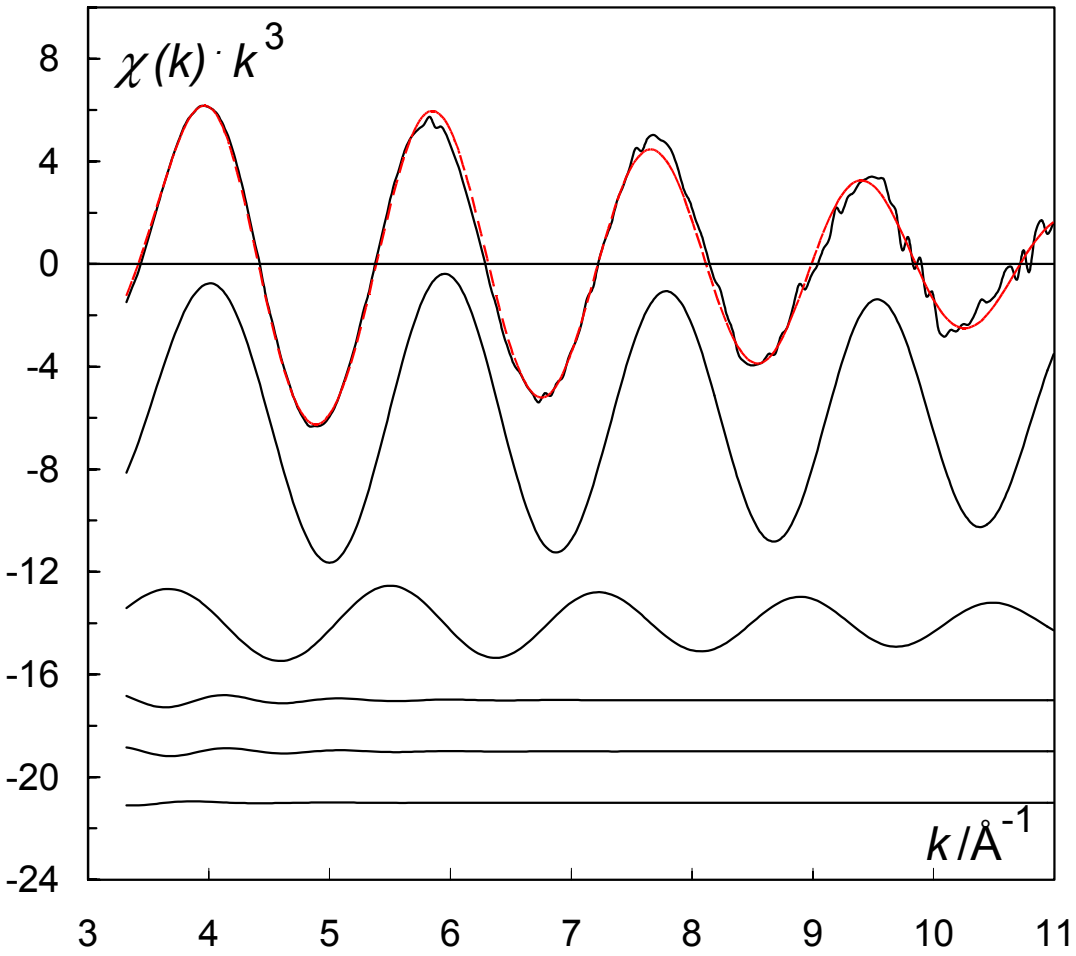


Fig. S1h.

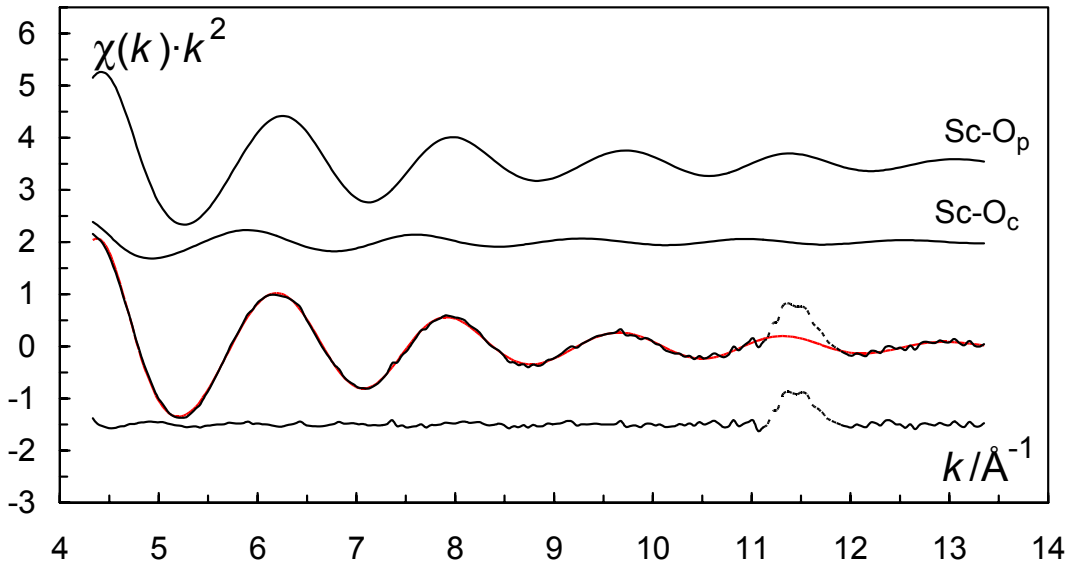


Fig. S1i.

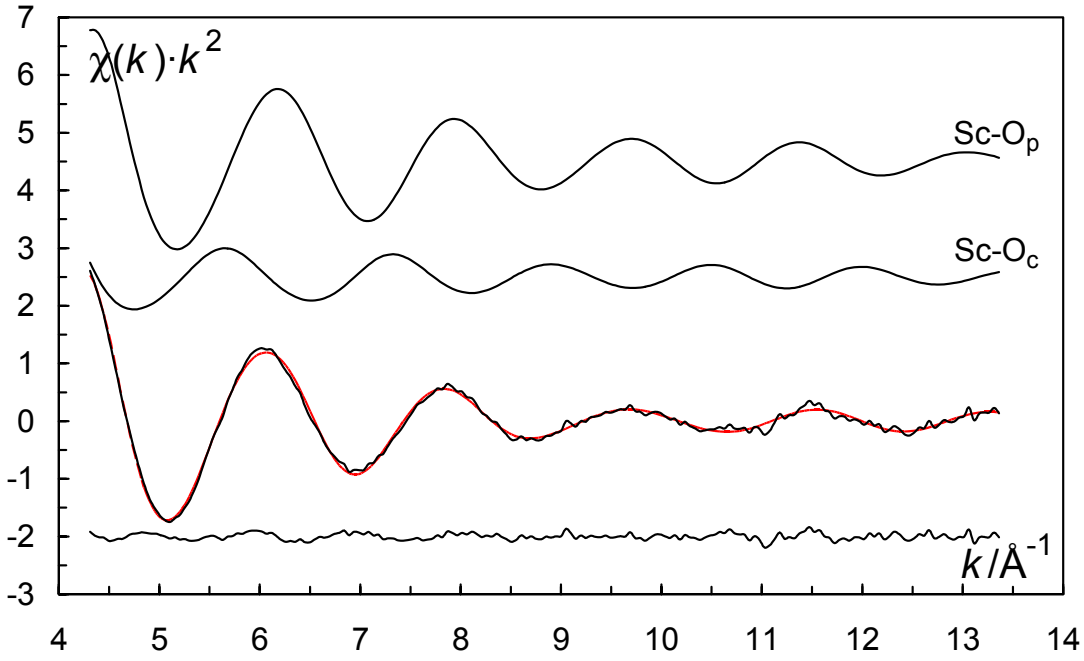
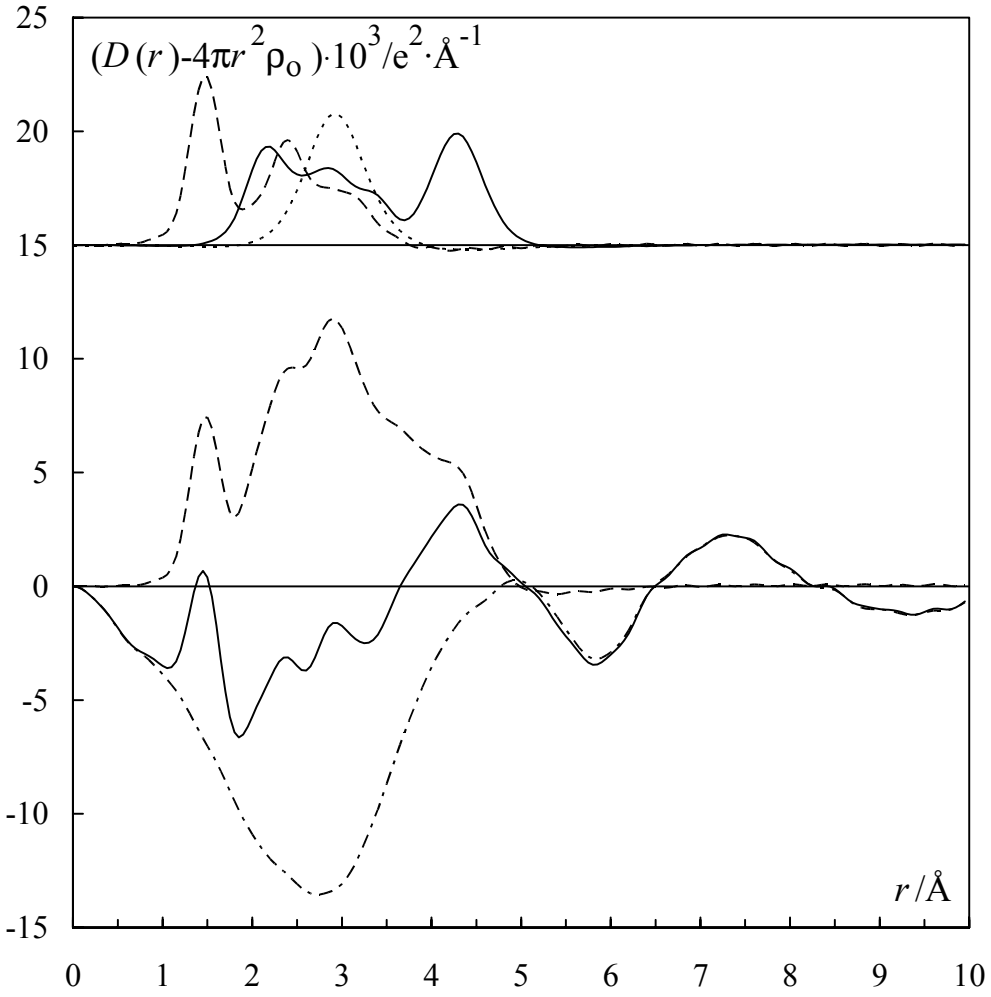


Fig. 2.


$(D(r)-4\pi r^2\rho_o)\cdot 10^3/e^2\cdot Å^{-1}$
r/Å
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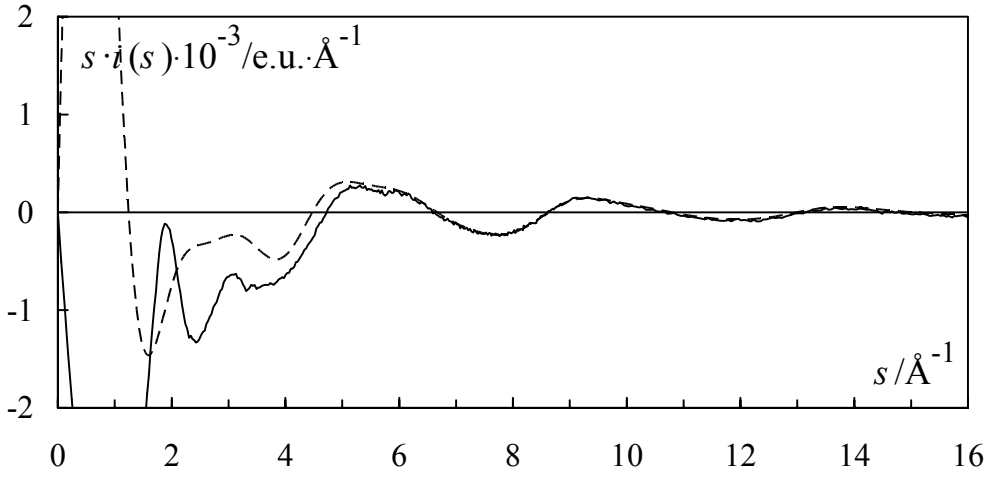
20
15
10
5
0
-5
-10
-15
0
1
2
3
4
5
6
7
8
9
10


$s\cdot i(s)\cdot 10^{-3}$/e.u.·Å^{-1}
s/Å^{-1}
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-1
-2
0
2
4
6
8
10
12
14
16

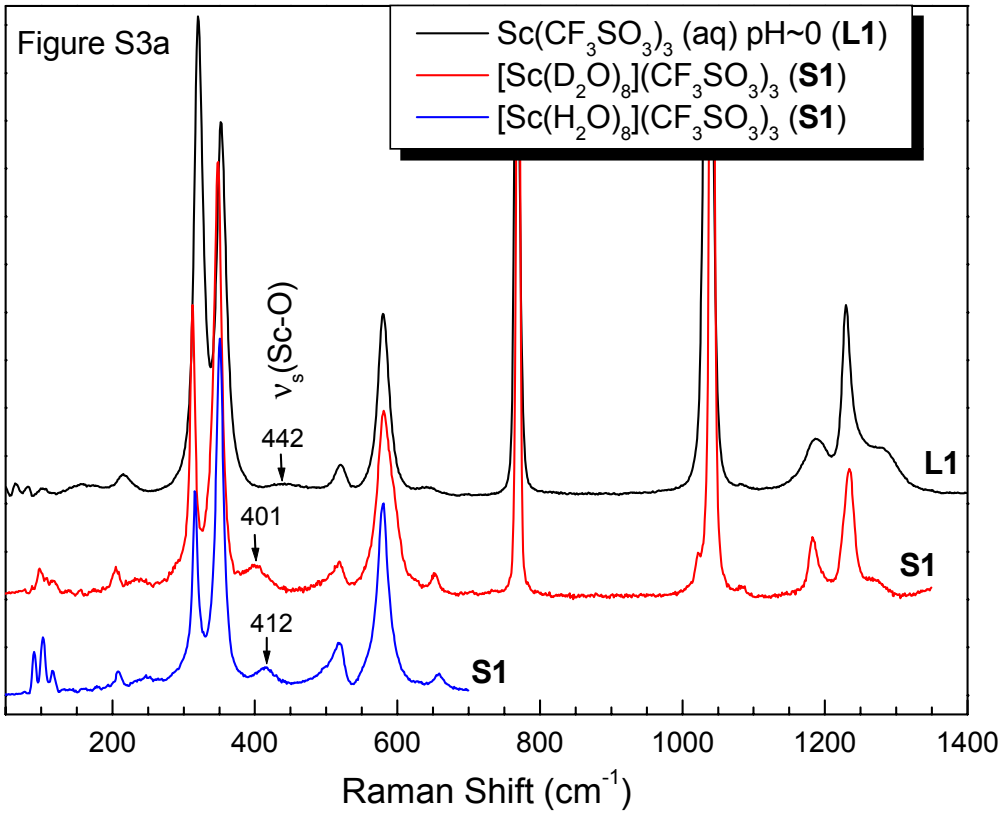
Figure S3a
Sc(CF3SO3)3 (aq) pH~0 (L1)
[Sc(D2O)8](CF3SO3)3 (S1)
[Sc(H2O)8](CF3SO3)3 (S1)
νs(Sc-O)
442
401
412
L1
S1
S1
200
400
600
800
1000
1200
1400
Raman Shift (cm-1)

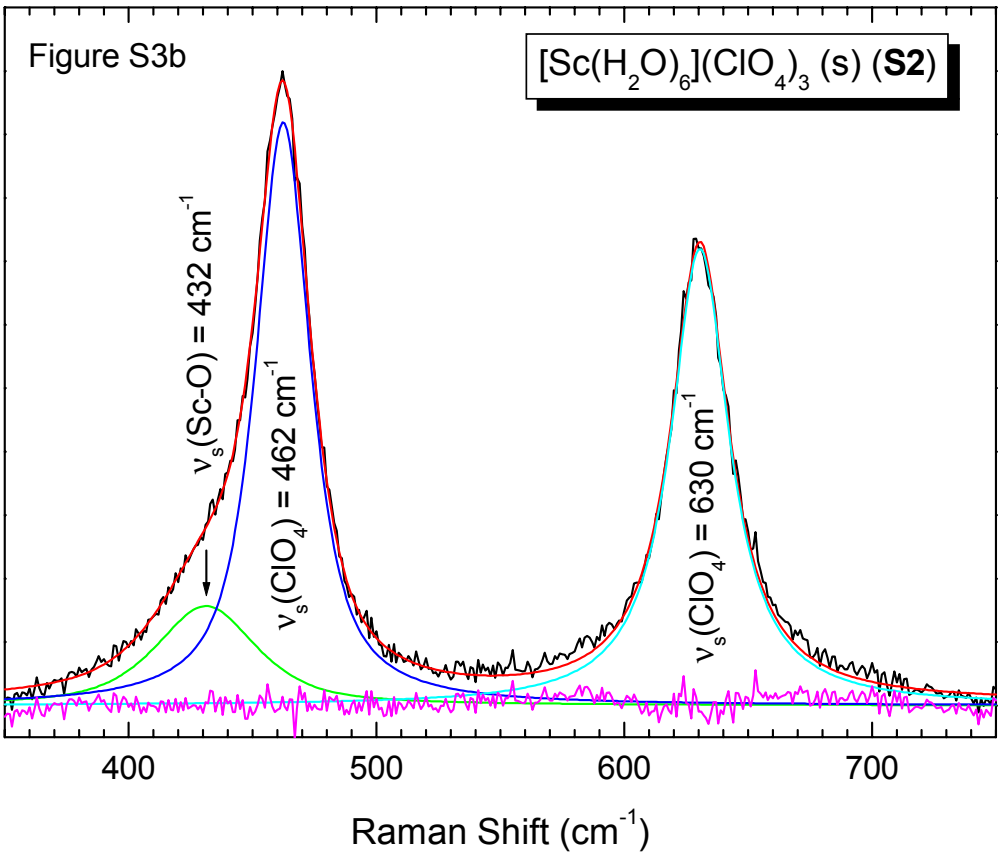
Figure S3b
[Sc(H2O)6](ClO4)3 (s) (S2)
νs(Sc-O) = 432 cm-1
νs(ClO4) = 462 cm-1
νs(ClO4) = 630 cm-1
400
500
600
700
Raman Shift (cm-1)

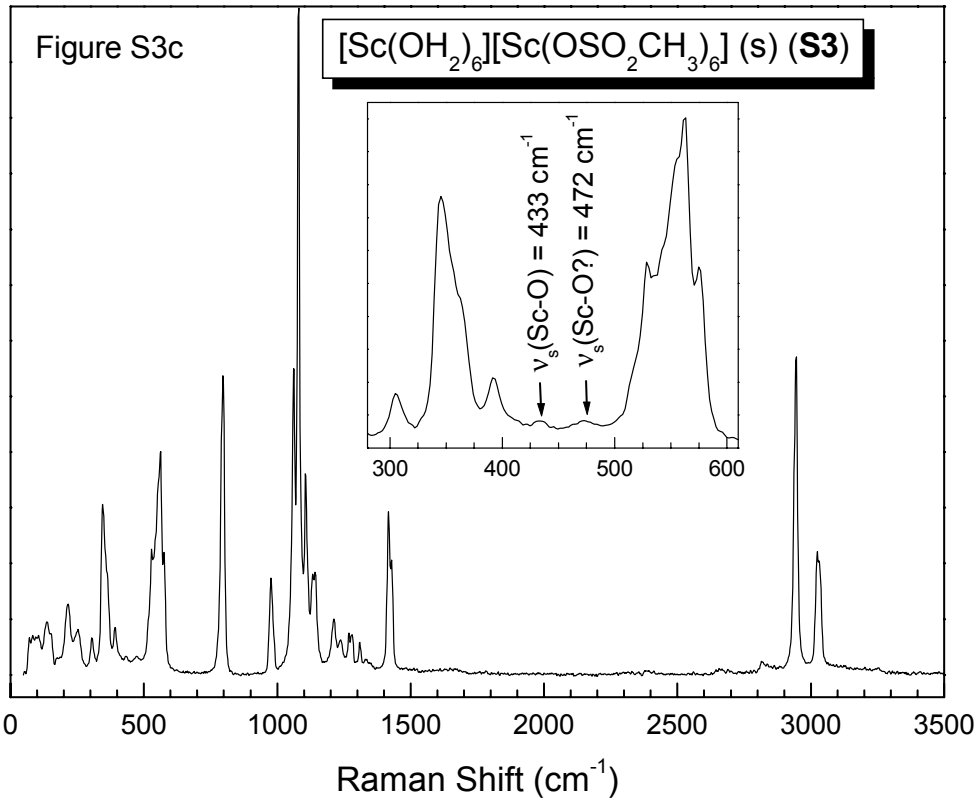
Figure S3c
[Sc(OH2)6][Sc(OSO2CH3)6] (s) (S3)
νs(Sc-O) = 433 cm-1
νs(Sc-O?) = 472 cm-1
300
400
500
600
0
500
1000
1500
2000
2500
3000
3500
Raman Shift (cm-1)

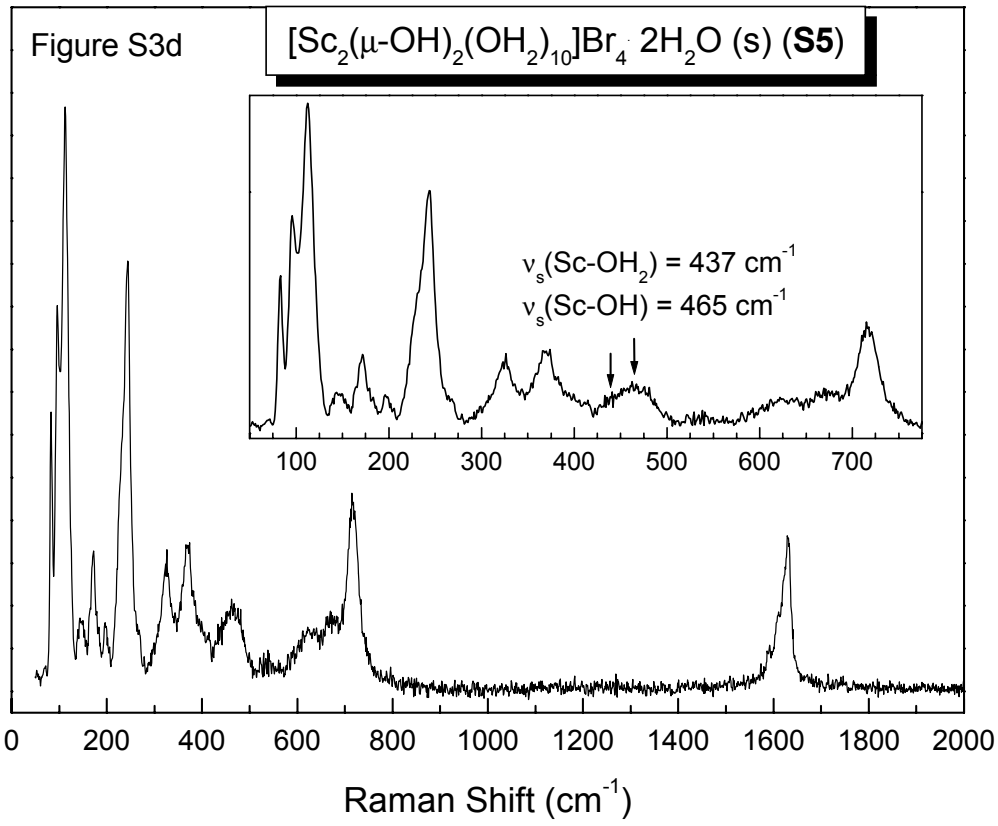
Figure S3d
[Sc2(μ-OH)2(OH2)10]Br4· 2H2O (s) (S5)
νs(Sc-OH2) = 437 cm-1
νs(Sc-OH) = 465 cm-1
100 200 300 400 500 600 700
0 200 400 600 800 1000 1200 1400 1600 1800 2000
Raman Shift (cm-1)

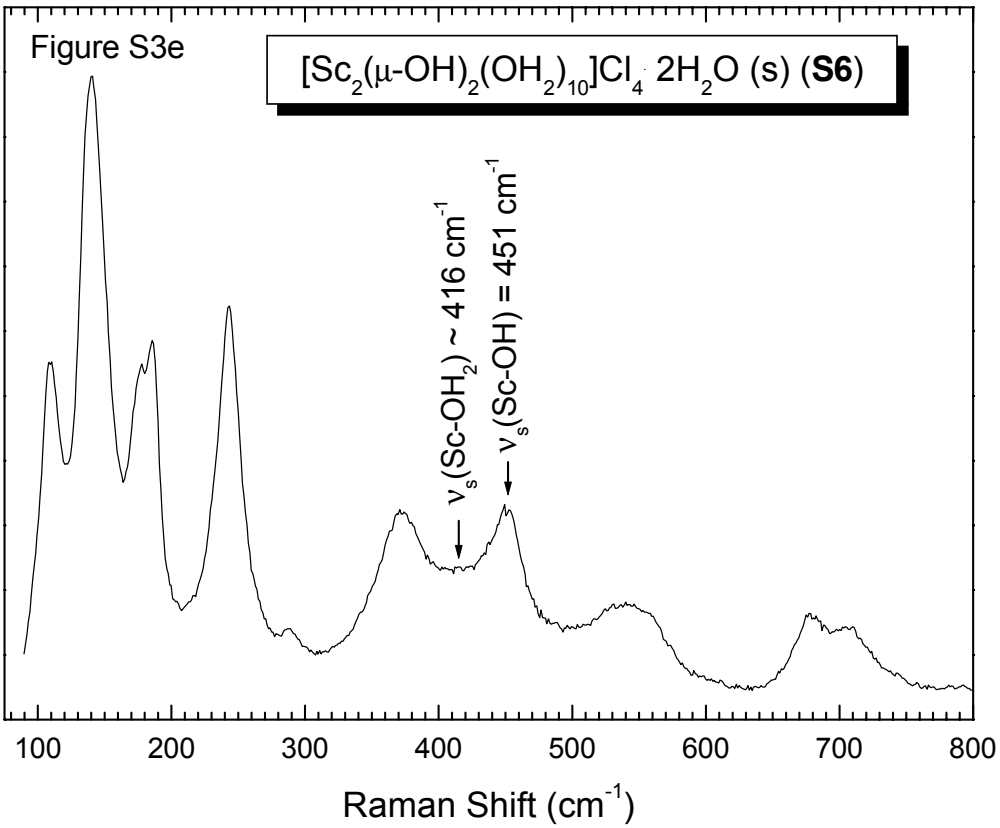
Figure S3e
[Sc2(μ-OH)2(OH2)10]Cl4· 2H2O (s) (S6)
νs(Sc-OH2) ~ 416 cm-1
νs(Sc-OH) = 451 cm-1
100 200 300 400 500 600 700 800
Raman Shift (cm-1)