Supplementary Material

Table S1. Normal modes (n.m.) of MnO_6 for group O_h, their description and correlation for the species of O_h group and its subgroups T_h and T including the activity in Raman and infrared.

n.m.	Description of vibration	O_h	T_h	T
ν_1	ν_s Mn-O	A_{1g} (R)	A_g (R)	A (R)
ν_2	ν Mn-O	E_g (R)	E_g (R)	E (R)
ν_3	ν Mn-O	F_{1u} (IR)	F_u (IR)	F (R,IR)
ν_4	δ O-Mn-O	F_{1u} (IR)	F_u (IR)	F (R,IR)
ν_5	δ O-Mn-O	F_{2g} (R)	F_g (R)	F (R,IR)
ν_6	δ O-Mn-O	F_{2u} (n.a.)	F_u (IR)	F (R,IR)

R = Raman allowed; IR: infrared active; n.a.: not allowed

Figure S2. DFT frequencies at the UB3LYP/ 6-311+G(d,p) level of theory for the octadeca-hydrate of Mn^{2+}, $[Mn(OH_2)_{18}]^{2+}$.

frequ. cm^{-1}	ín D2O			mode	frequ. cm^{-1}	in D2O			
29.9		F	i.r. Ra	rot. $(H_2O)_3$	565.2		A	Ra	τ,ρ HOH
42.8		E	Ra	trans. $(H_2O)_3$	587.0		F	i.r. Ra	τ,ρ HOH
43.8		A	Ra	rot. $(H_2O)_3$	620.1		A	Ra	τ,ρ HOH
51.5		F	i.r. Ra	trans. $(H_2O)_3$,MnO_6	652.1		F	i.r. Ra	ω,τ HOH
74.8		F	i.r. Ra	δ OMnO + trans. H_2O	671.5		E	Ra	τ HOH
87.8	84.2	F	i.r. Ra	δ OMnO + trans. H_2O	699.4		F	i.r. Ra	ω,τ HOH
102.4	97.2	F	i.r. Ra	δ OMnO + trans. H_2O	774.3		F	i.r. Ra	ρ,τ HOH
115.3		E	Ra	ν_s OMnO + trans. H_2O	820.1		F	i.r. Ra	ρ,τ HOH
132.5	124.6	F	i.r. Ra	δ OMnO + trans. H_2O	853.9		A	Ra	ω HOH
142.5		F	i.r. Ra	δ OMnO + trans. H_2O	857.2		F	i.r. Ra	ω HOH
145.2		A	Ra	trans. $(H_2O)_3$	1633.3		F	i.r. Ra	δ HOH
157.1		F	i.r. Ra	δ OMnO + trans. H_2O	1634.0		E	Ra	δ HOH
183.6		F	i.r. Ra	δ OMnO + trans. H_2O	1634.2		F	i.r. Ra	δ HOH
184.3		E	Ra	trans. H_2O	1634.8		F	i.r. Ra	δ HOH
205.1		F	i.r. Ra	trans. H_2O	1635.3		A	Ra	δ HOH
205.8		A	Ra	trans. H_2O	1697.8		E	Ra	δ HOH
236.4		F	i.r. Ra	δ OMnO + trans. H_2O	1701.9		F	i.r. Ra	δ HOH
248.3		F	i.r. Ra	δ OMnO + trans. H_2O	1715.1		A	Ra	δ HOH
281.9	280.6	E	Ra	ν_s Mn-O	3560.2		E	Ra	ν_s OH
334.8		F	i.r. Ra	ρ HOH	3568.1		F	i.r. Ra	ν_s OH
339.0	328.3	A	Ra	ν_s Mn-O	3597.4		A	Ra	ν_s OH
339.1		F	i.r. Ra	ρ HOH+ν_{as} Mn-O	3600.3		F	i.r. Ra	ν_s,ν_{as} OH
348.8	326.4	F	i.r. Ra	ν_{as} Mn-O	3604.9		F	i.r. Ra	ν_s,ν_{as} OH
351.3	341.9	E	Ra	ρ HOH	3609.5		A	Ra	ν_s OH
398.3	370.4	F	i.r. Ra	ρ HOH +ν_{as} OMnO	3638.3		F	i.r. Ra	ν_s,ν_{as} OH
418.7		A	Ra	ω HOH	3662.6		E	Ra	ν_s OH
442.1		F	i.r. Ra	ρ,ω HOH	3669.7		F	i.r. Ra	ν_s,ν_{as} OH
463.7		F	i.r. Ra	ρ,τ HOH	3675.5		F	i.r. Ra	ν_{as},ν_s OH
467.8		E	Ra	ρ HOH	3854.2		F	i.r. Ra	ν_{as} OH
511.2		F	i.r. Ra	τ HOH	3854.7		F	i.r. Ra	ν_{as} OH
520.9		F	i.r. Ra	ω HOH	3854.8		E	Ra	ν_{as} OH
542.2		E	Ra	τ HOH	3858.3		F	i.r. Ra	ν_{as} OH
550.5		F	i.r. Ra	ρ,τ HOH	3859.0		A	Ra	ν_{as} OH

ν_s: symmetric stretching, ν_{as}: antisymmetric stretching, δ: deformating, ρ: rocking, ω: wagging, τ: twisting; rot. and trans. means restricted rotations and translations

Table S3. DFT frequencies at the UB3LYP/ 6-311+G(d,p) level of theory for the octadeca-hydrate of Mn^{2+}, $[Mn(OH_2)_{18}]^{2+}$ with solvation shell (PCM model).

frequ. cm^{-1}	ín D2O			mode	frequ. cm^{-1}	in D2O			
13.6		F	i.r. Ra	rot. $(H_2O)_3$	510.6		E	Ra	ω,τ HOH
30.8		A	Ra	rot. $(H_2O)_3$	573.9		F	i.r. Ra	ω,τ HOH
39.0		E	Ra	trans. $(H_2O)_3$	610.9		F	i.r. Ra	ω,τ HOH
39.9		F	i.r. Ra	trans. $(H_2O)_3$,MnO_6	627.2		A	Ra	τ HOH
62.4		F	i.r. Ra	δ OMnO + trans. H_2O	655.7		F	i.r.Ra	τ HOH
76.2		F	i.r. Ra	δ OMnO + rot. H_2O	680.5		E	Ra	τ HOH
81.5		F	i.r. Ra	δ OMnO + rot. H_2O	735.7		F	i.r. Ra	τ HOH
83.8		E	Ra	ν_s OMnO + rot. H_2O	740.1		A	Ra	τ HOH
93.6	86.7	F	i.r. Ra	δ OMnO + trans. H_2O	786.3		F	i.r.Ra	ρ,τ HOH
109.3	103.3	F	i.r. Ra	δ OMnO + trans. H_2O	842.8		F	i.r. Ra	ρ,τ HOH
133.8		E	Ra	ν_s OMnO + rot. H_2O	1559.1		F	i.r. Ra	δ HOH
141.9	136.7	F	i.r. Ra	δ OMnO + trans. H_2O	1559.5		E	Ra	δ HOH
155.9		A	Ra	trans. H_2O	1559.5		F	i.r. Ra	δ HOH
160.7		F	i.r. Ra	δ OMnO + trans. H_2O	1566.9		A	Ra	δ HOH
187.6		F	i.r. Ra	trans. H_2O	1567.9		F	i.r. Ra	δ HOH
187.8		A	Ra	trans. H_2O	1674.9		E	Ra	δ HOH
232.9		F	i.r. Ra	δ OMnO + rot. H_2O	1683.1		F	i.r. Ra	δ HOH
241.5		F	i.r. Ra	δ OMnO + rot. H_2O	1703.1		A	Ra	δ HOH
249.0		E	Ra	δ OMnO + rot. H_2O	3488.9		E	Ra	ν_s OH
254.8		F	i.r. Ra	δ OMnO + rot. H_2O	3495.3		F	i.r. Ra	ν_s OH
258.2		F	i.r. Ra	δ OMnO + rot. H_2O	3523.4		A	Ra	ν_s OH
299.5	287.0	E	Ra	ν_s Mn-O	3529.5		F	i.r. Ra	ν_s,ν_{as} OH
313.3		A	Ra	ν_s Mn-O + ρ HOH	3533.9		F	i.r. Ra	ν_s,ν_{as} OH
313.6		F	i.r. Ra	ρ HOH	3580.5		A	Ra	ν_s OH
342.3		F	i.r. Ra	ν_{as} Mn-O + ρ HOH	3586.0		F	i.r. Ra	ν_s OH
346.6		F	i.r.Ra	ρ HOH	3599.0		E	Ra	ν_s OH
359.3	329.1	A	Ra	ν_s Mn-O	3602.2		F	i.r. Ra	ν_s,ν_{as} OH
361.3		E	Ra	ρ, ω HOH	3605.0		F	i.r. Ra	ν_s,ν_{as} OH
364.4	328.4	F	i.r. Ra	ν_{as} Mn-O + ρ, ω HOH	3659.0		A	Ra	ν_{as} OH
463.9		F	i.r. Ra	ρ, ω HOH	3695.2		F	i.r. Ra	ν_{as} OH
479.2		F	i.r. Ra	ρ, ω HOH	3670.7		E	Ra	ν_{as} OH
492.3		A	Ra	ρ HOH	3671.2		F	i.r. Ra	ν_{as} OH
500.9		F	i.r. Ra	ρ,τ HOH	3672.1		F	i.r. Ra	ν_{as} OH

ν_s: symmetric stretching, ν_{as}: antisymmetric stretching, δ: deforming, ρ: rocking, ω: wagging, τ: twisting; rot. and trans. means restricted rotations and translations

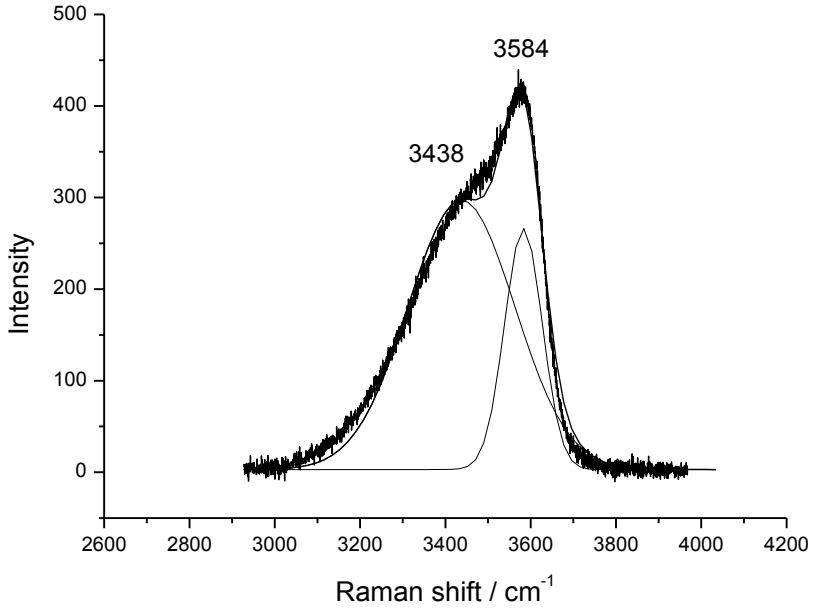

Figure S1. Isotropic Raman band ν O-H stretch of HDO/D_2O of a 1.96 molL^{-1} $Mn(ClO_4)_2$ in heavy water with 2% HDO. Given are both component bands at 3438 cm^{-1} and at 3584 cm^{-1}**.**

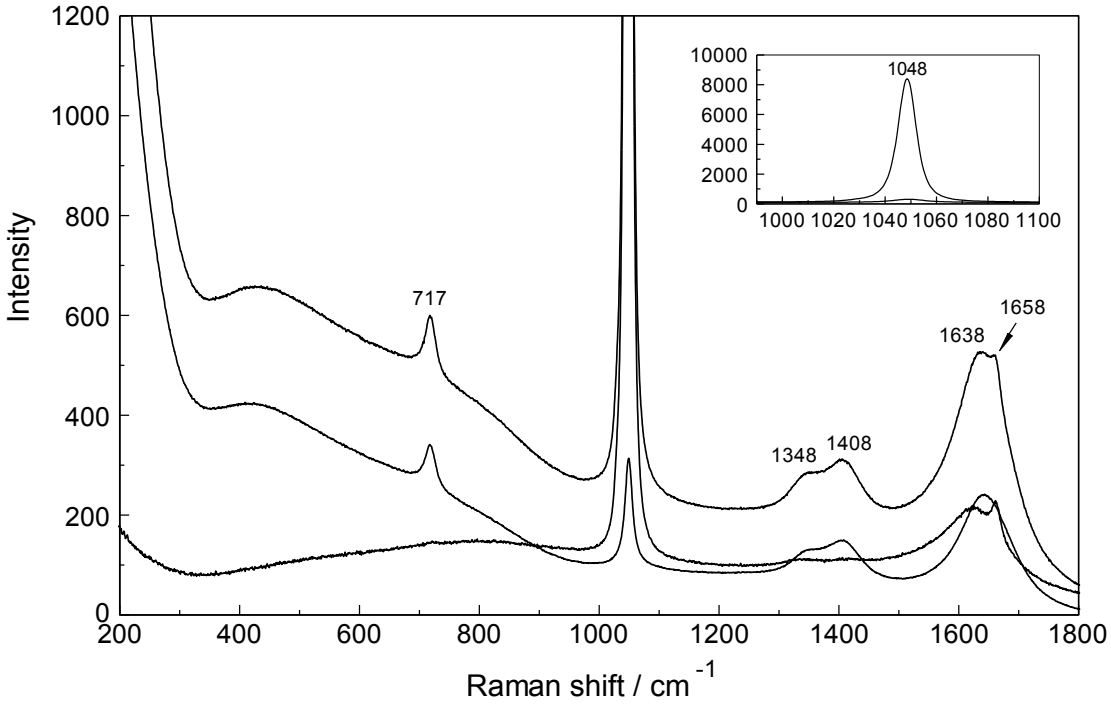

Figure S2. Raman spectrum (polarized, depolarized and isotropic scattering is given) of an aqueous 0.0409 mol·L^{-1} $NaNO_3$ solution. The nitrate bands are explained in the text. Note, that the sharp band at 1658 cm^{-1} is due to an overtone of NO_3^-, 2 x ν_2 and the broad band at 1638 cm^{-1} is due to δ H_2O.

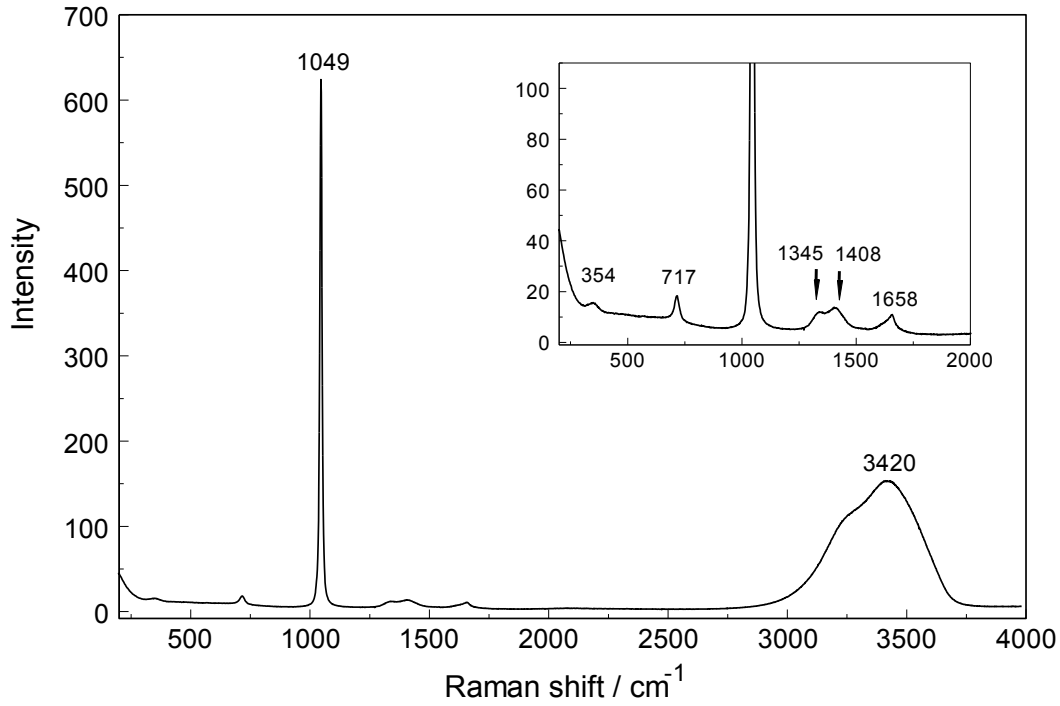

Figure S3. Polarized overview Raman spectrum of a 1.73 molL^{-1} $Mn(NO_3)_2$ solution at 23 °C. The inset shows the wavenumber region from 200-2000 cm^{-1} at an enlarged scale. The nitrate bands are explained in the text. Note, that the sharp band at 1659 cm^{-1} is due to an overtone of NO_3^-, 2 x ν_2, overlapping the water mode, δ H_2O at 1638 cm^{-1} almost completely. The very broad O-H stretching mode of H_2O peaks at 3420 cm^{-1}.