Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Materials Section

Wolfram W. Rudolph and Gert Irmer: "Raman spectroscopic characterization of light rare earth ions: La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} - Hydration and ion pair formation."
Dalton Trans., 02/2017

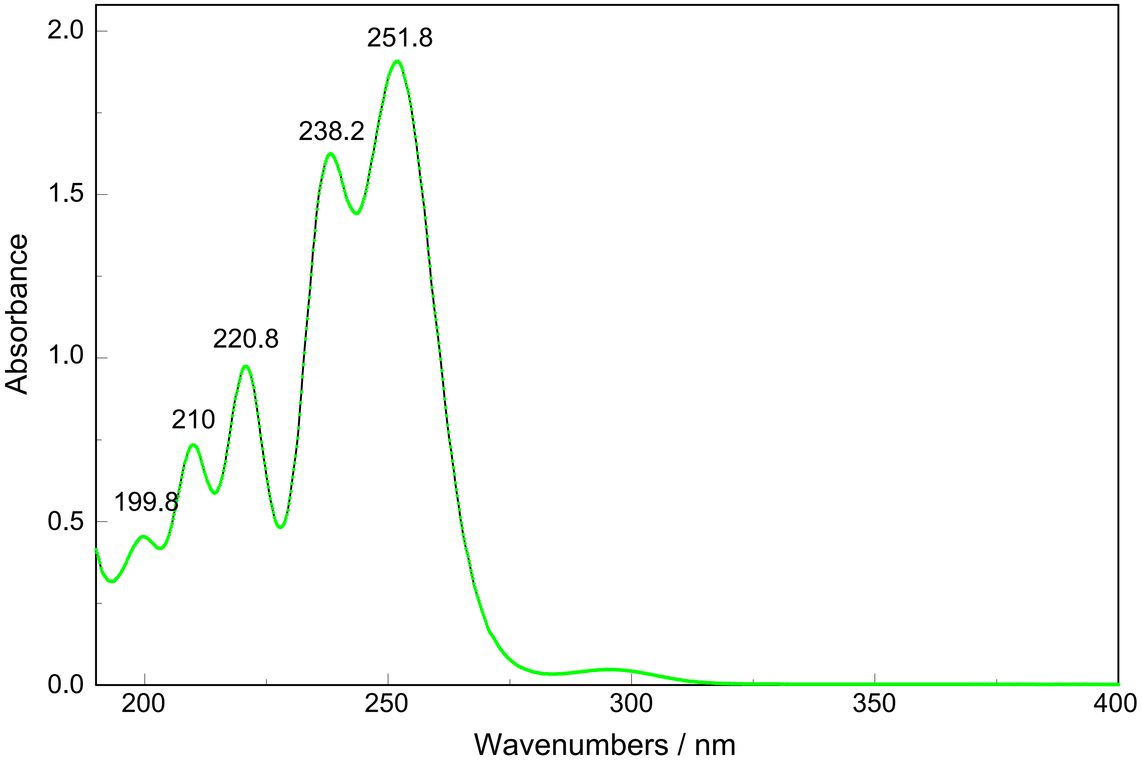

Figure S1A. UV absorption spectrum of an aqueous 0.0025 $molL^{-1}$ $Ce(ClO_4)_3$ solution at 22 °C. Shown are the five characteristic UV bands of $Ce^{3+}(aq)$. Note the small contribution at 296.4 nm.

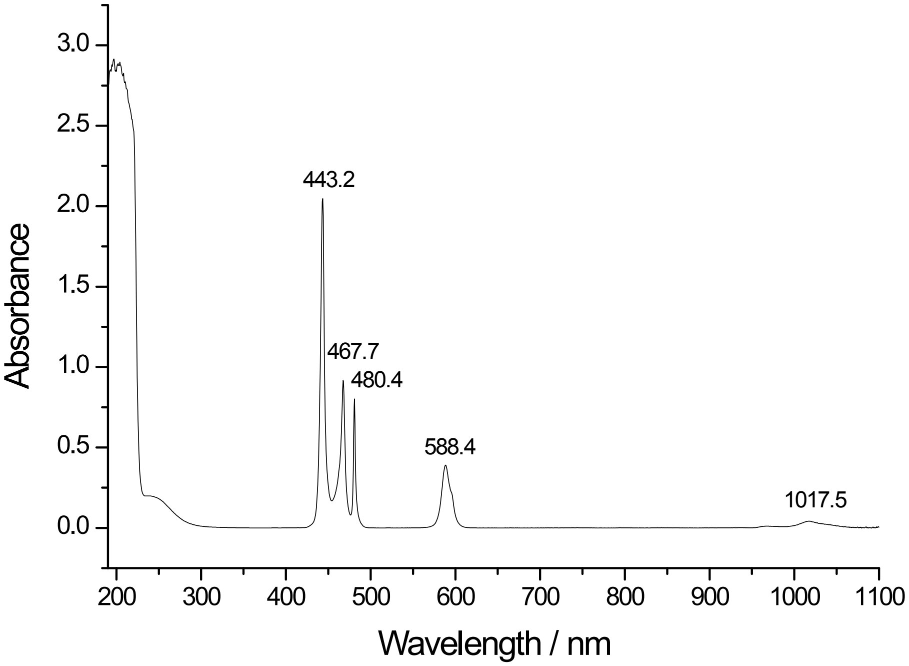

Figure S1B. UV/UV-vis absorption spectrum of an aqueous 0.317 molL^{-1} Pr(ClO$_4$)$_3$ solution at 22 °C.

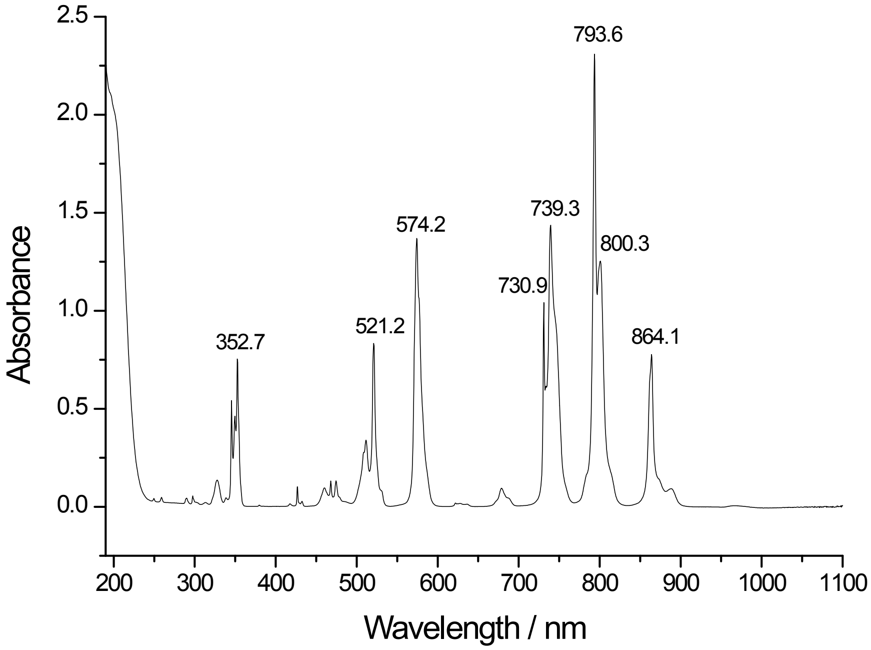

Figure S1C. UV/UV-vis absorption spectrum of an aqueous 0.256 molL^{-1} Nd(ClO$_4$)$_3$ solution at 22 °C.

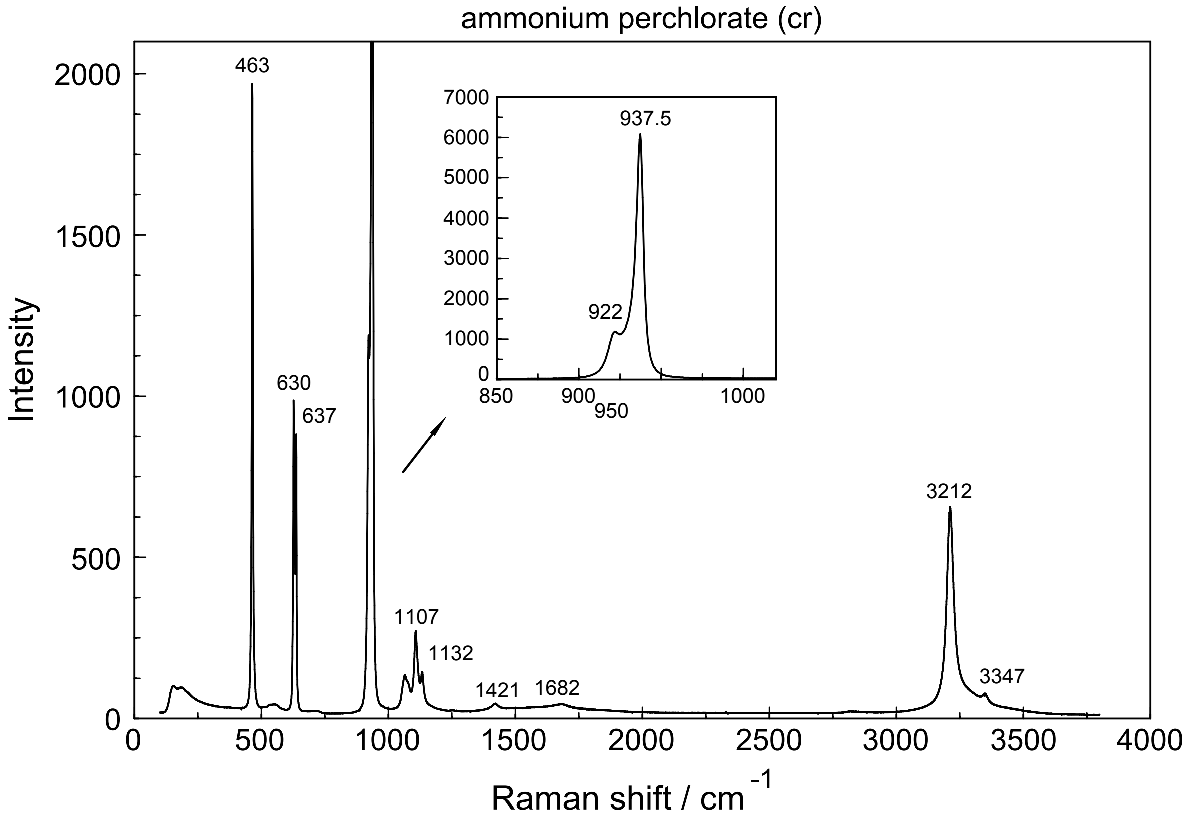

Figure S2. Raman spectrum of crystalline NH_4ClO_4 at 22 °C Note, that not all band positions are given. The inset shows the ν_1 ClO_4^- band in full detail. Note the band split into two components at 922 cm^{-1} and 937.5 cm^{-1}. The band at 922 cm^{-1} is due to Fermi resonance.

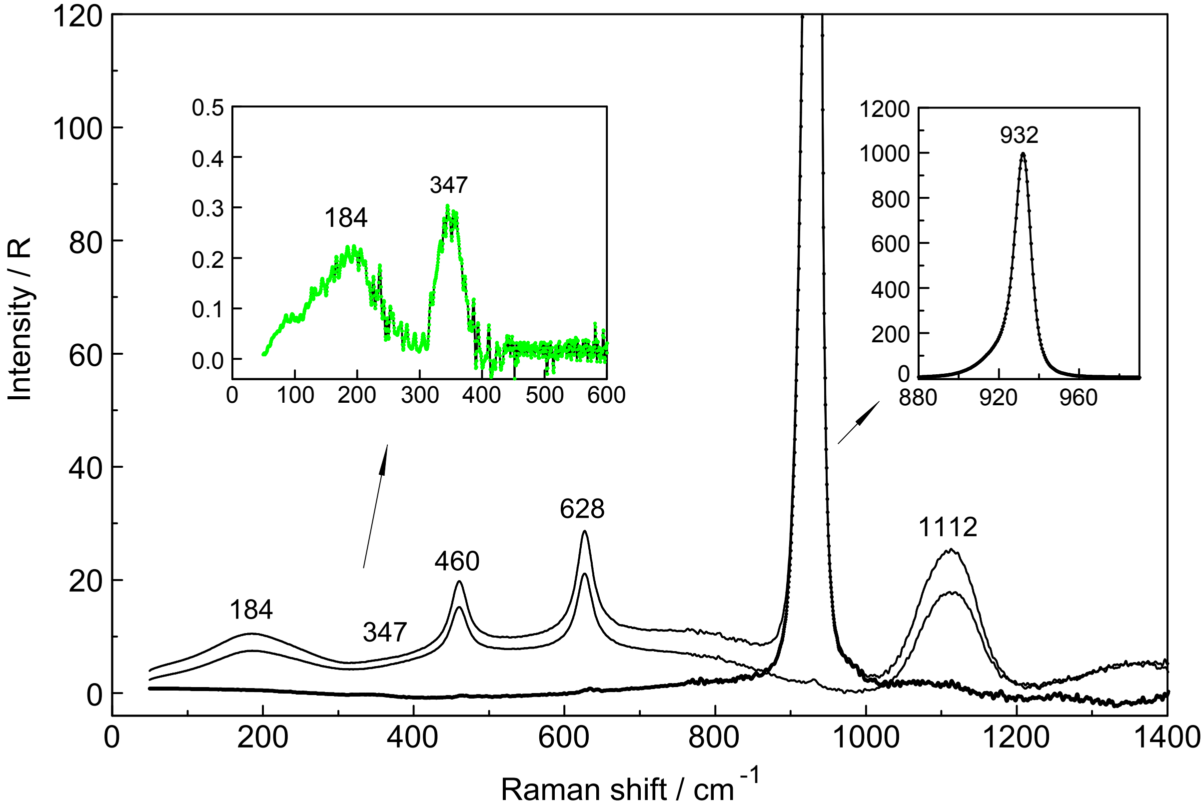

Figure S3. Raman scattering profiles (from top to bottom: R_{VV}, R_{VH} and R_{ios}) of a 0.317 molL^{-1} $Pr(ClO_4)_3$ solution at 22 °C. Left inset: Isotropic profile of the low frequency region shows the ν_1 Pr-O breathing mode at 347 cm^{-1} in detail. Right inset: The isotropic band profile of the ν_1 ClO_4^- mode at 932.15 cm^{-1} at full scale

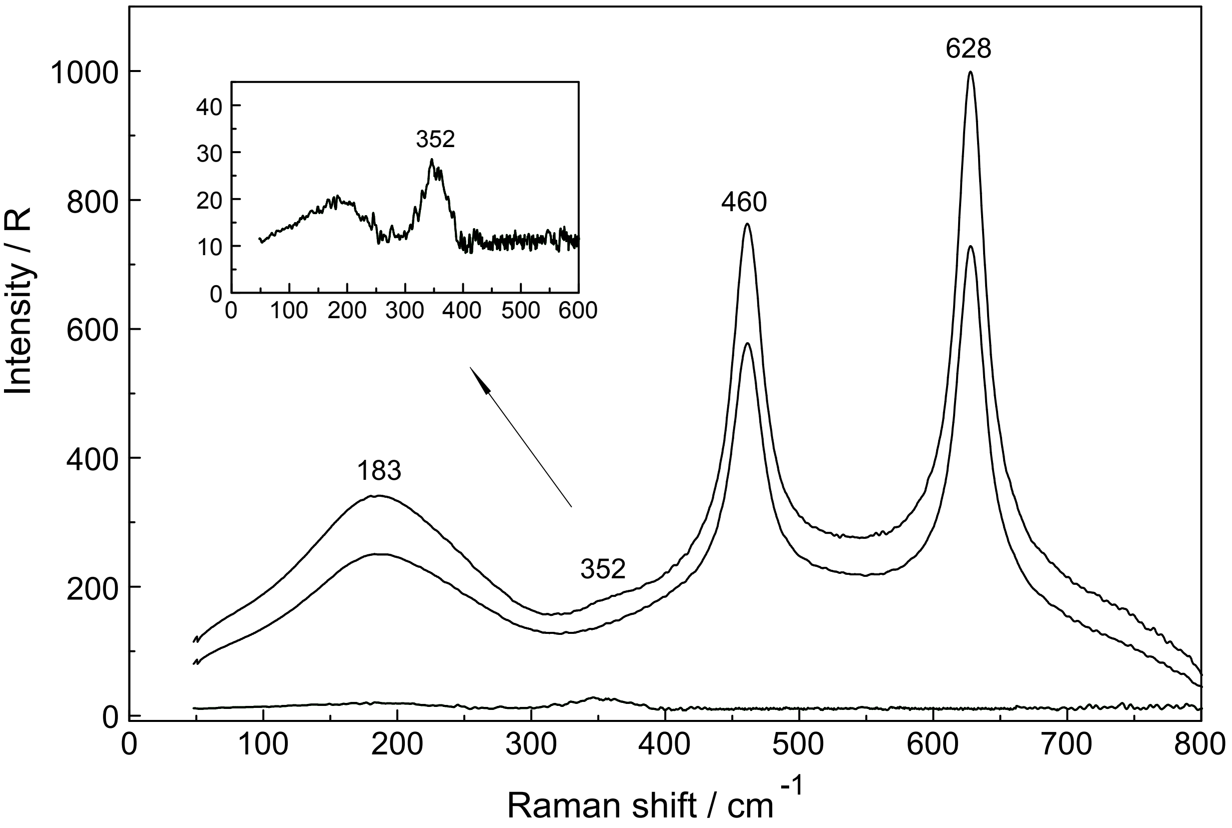

Figure S4. Raman scattering profiles (from top to bottom: R_{VV}, R_{VH} and R_{ios}) of a 0.256 molL^{-1} $Nd(ClO_4)_3$ solution at 22 °C. Inset: Isotropic profile of the low frequency region showing the ν_1 Nd-O breathing mode at 352 cm^{-1}.

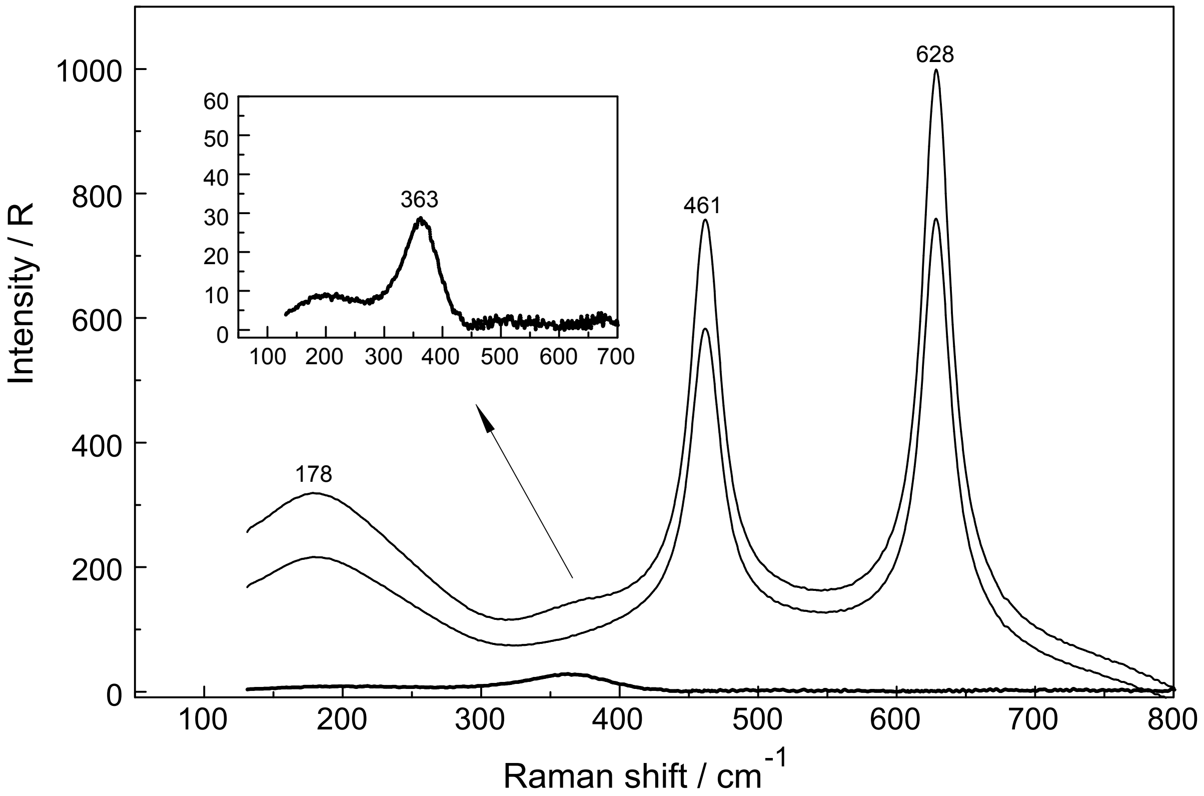

Figure S5. Raman scattering profiles (from top to bottom: R_{VV}, R_{VH} and R_{ios}) of a 0.274 molL^{-1} $Sm(ClO_4)_3$ solution at 22 °C. Inset: Isotropic profile of the low frequency region showing the ν_1 Sm-O breathing mode at 363 cm^{-1}.

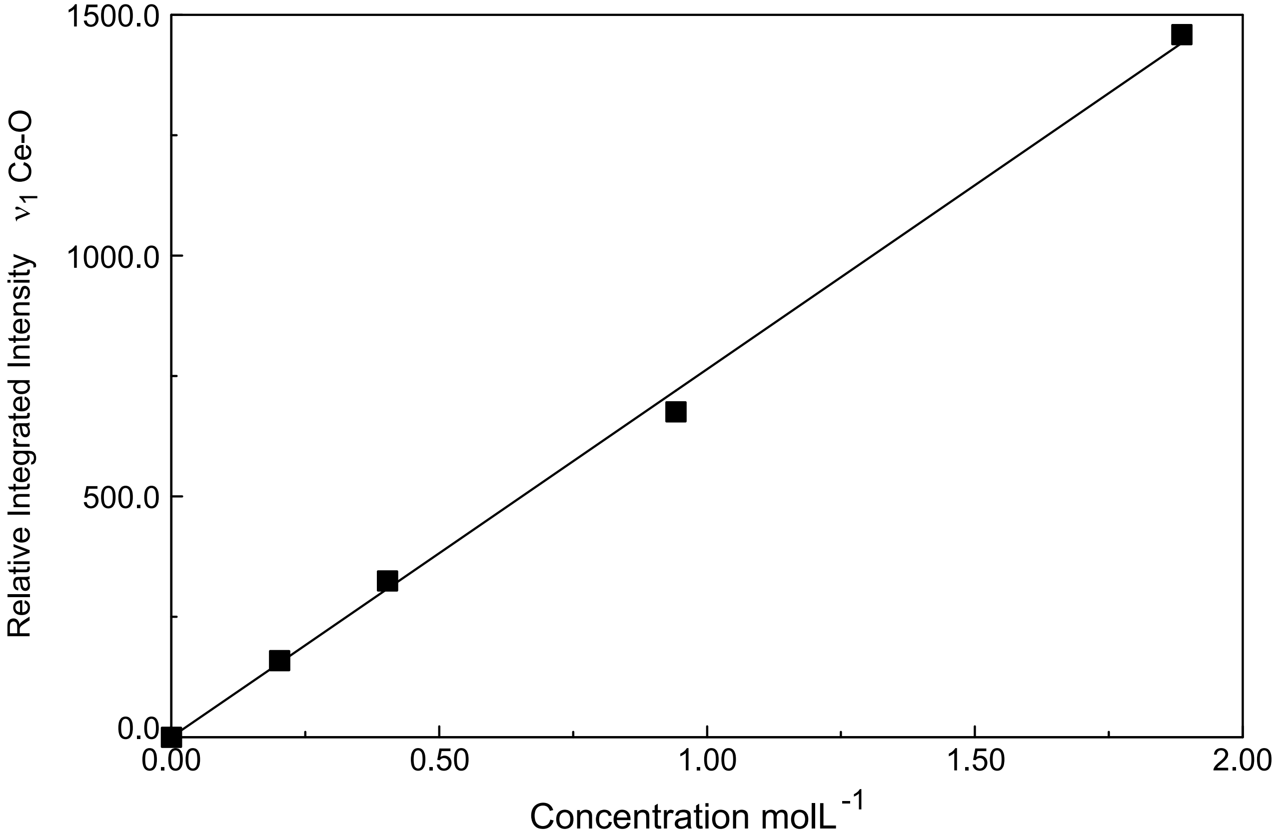

Figure S6. Concentration plot of the integrated band intensity of the breathing mode ν_1 Ce-O in $Ce(ClO_4)_3$(aq). Concentrations of $Ce(ClO_4)_3$: at 0.202, 0.404, 0.942, and 1.889 molL^{-1} ($R^2 = 0.998$).

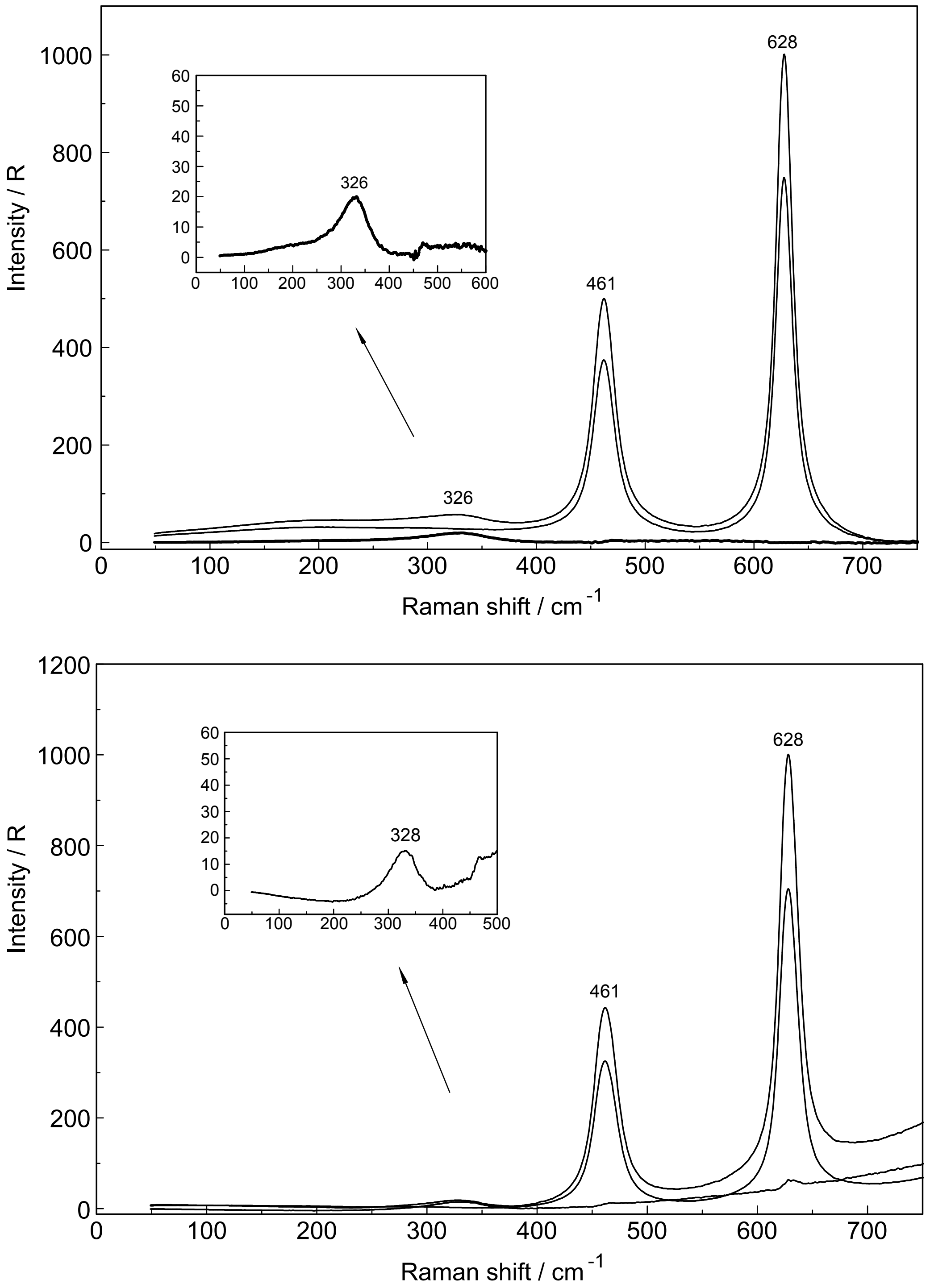

Figure S7. Upper panel: Raman scattering profiles (R_{VV}, R_{VH} and R_{iso}, with slightly thicker line) of a 1.281 molL^{-1} $Ce(ClO_4)_3$ solution in heavy water at 22 °C. Inset: Isotropic profile (R_{iso}) of the low frequency region showing the ν_1 Ce-O breathing mode at 326 cm^{-1} of the $[Ce(OD_2)_9]^{3+}$ species. Lower panel: The same scattering profiles of a 2.562 molL^{-1} $Ce(ClO_4)_3$ solution in heavy water. Inset: Isotropic profile (R_{iso}) of the terahertz frequency region showing the ν_1 Ce-O breathing mode at 328 cm^{-1} of the $[Ce(OD_2)_9]^{3+}$ species.

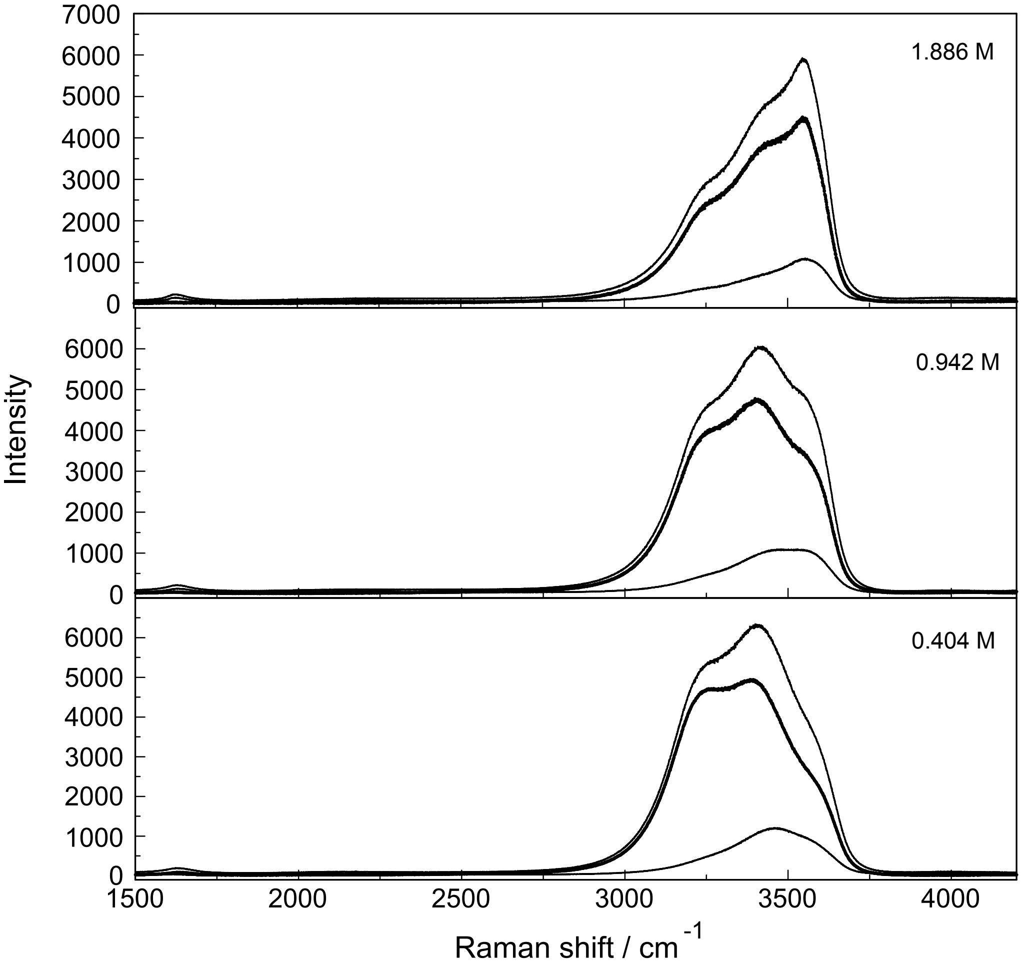

Figure S8. Raman scattering profiles (From top to bottom: I_{VV}, I_{iso}, and underneath I_{VH}; not that I_{iso} with slightly thicker line) of aqueous $Ce(ClO_4)_3$ solutions in the water deformation and O-H stretch region from1500 – 4200 cm^{-1}. Note the evolution of the mode at 3548 cm^{-1} with increasing $Ce(ClO_4)_3$ concentration. This mode is due to weak, decoupled O-H stretching modes (weak H-bonds: $H\text{-}OH\cdots OClO_3^-$). The broad water bands at 3235 and 3400 cm^{-1} diminishes with increasing $Ce(ClO_4)_3$ concentration.

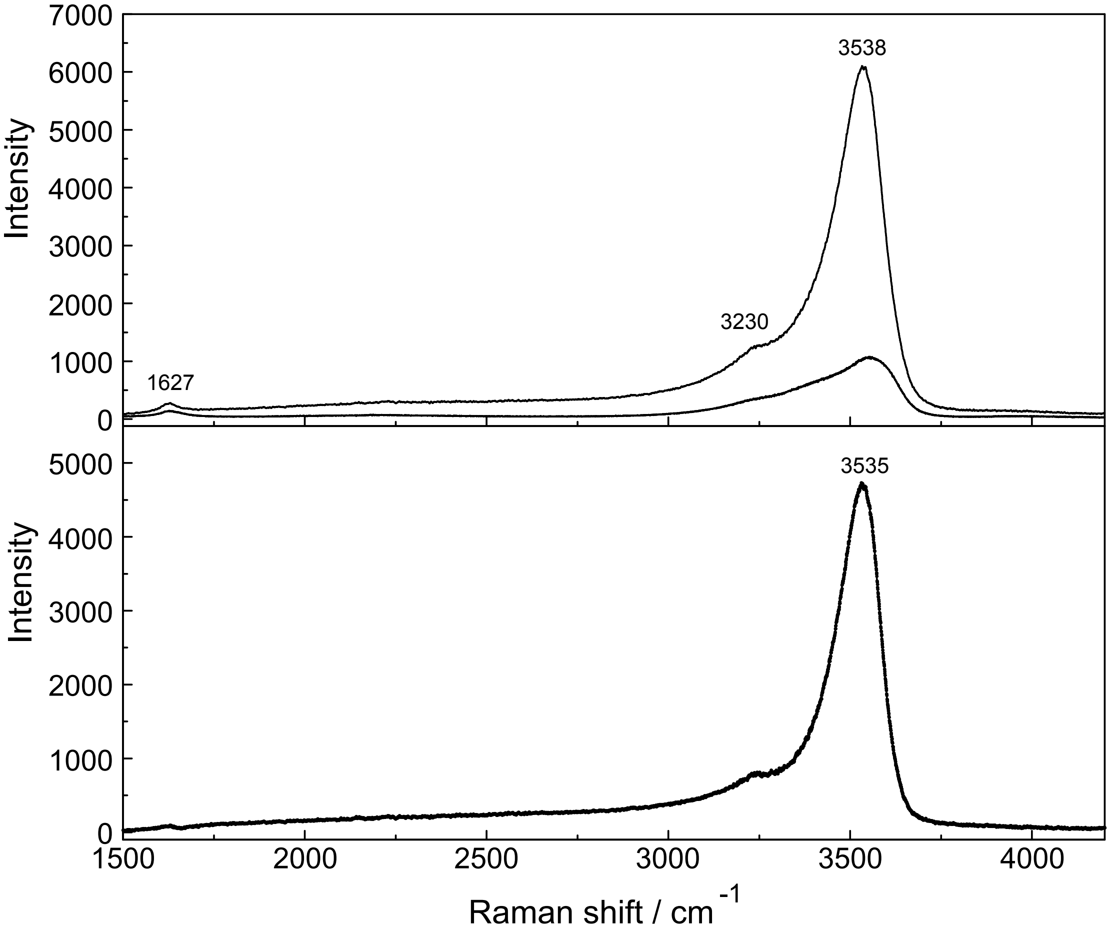

Figure S9. Raman scattering profiles of a 3.118 molL^{-1} Ce(ClO$_4$)$_3$ solution in wavenumber region from1500 – 4200 cm^{-1}. Upper panel shows the I_{VV} and I_{VH} scattering profiles. The weak band at 1627 cm^{-1} is due to the deformation mode of water and the mode at 3230 cm^{-1} the Fermi resonance component of the weak and very broad O-H stretching profile. The dominant band at 3538 cm^{-1} is due to the stretching band of water forming very weak H-bonds with ClO$_4^-$ (O-H····OClO$_3^-$). The lower panel shows the isotropic scattering component.

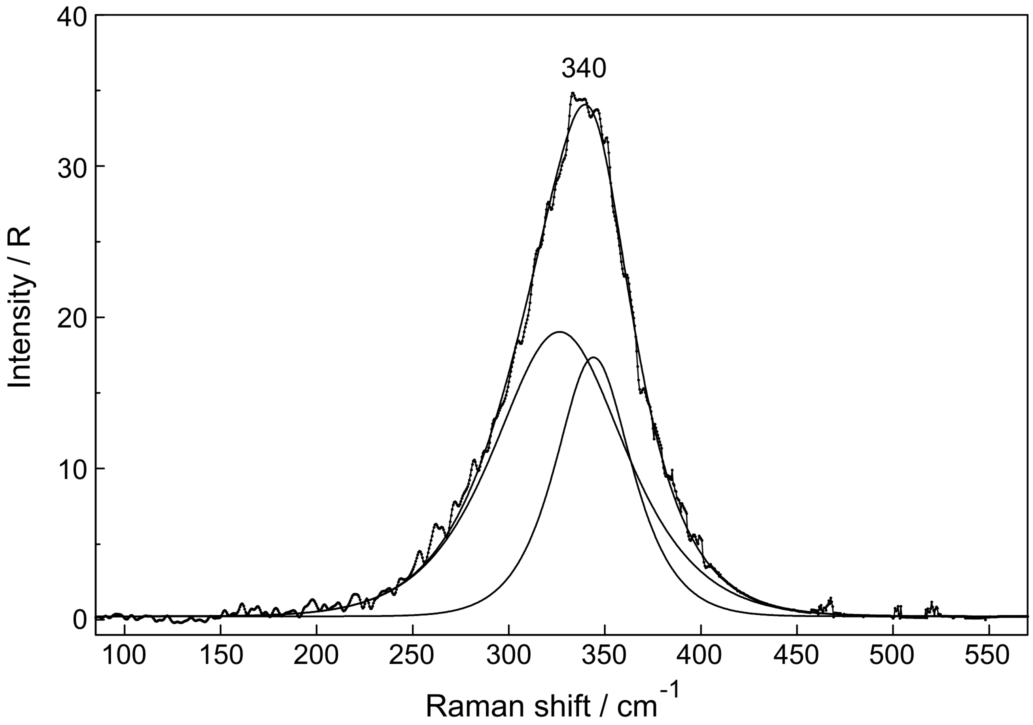

Figure S10. Isotropic Raman spectrum, R_{iso}, of a 3.118 molL^{-1} Ce(ClO$_4$)$_3$ in terahertz region at 22°C. The ν_1 Ce-O breathing mode is broad and peaks at 340 cm^{-1}. Given are the measured Raman spectrum, the sum curve of the fit and the two band components at 327 cm^{-1} and 344 cm^{-1}.

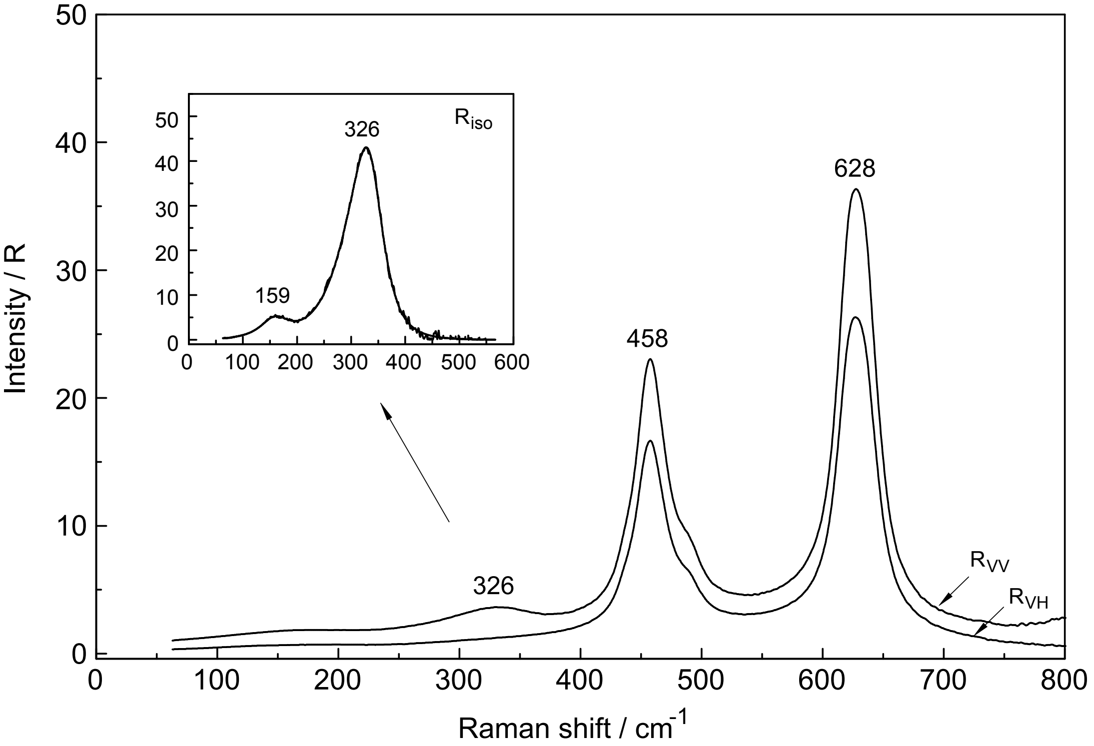

Figure S11A. Raman scattering profiles in R-format (R_{VV} and R_{VH}) of the $Ce(ClO_4)_3$ hydrate melt ($Ce(ClO_4)_3$ plus 6 H_2O) at 161°C in the low frequency region (60-800 cm^{-1}). The deformation modes of ClO_4^- at 458 cm^{-1} and 628 cm^{-1} are the prominent bands in the spectrum. (The polarized band profiles, R_{VV}, for both deformation modes including the sum curve of the fit and the components are given in greater detail in Figs. S11B and C further below.) The inset shows the R_{iso} scattering profile in the terahertz frequency region in larger detail (ν_1 Ce-O breathing mode at 326 cm^{-1}).

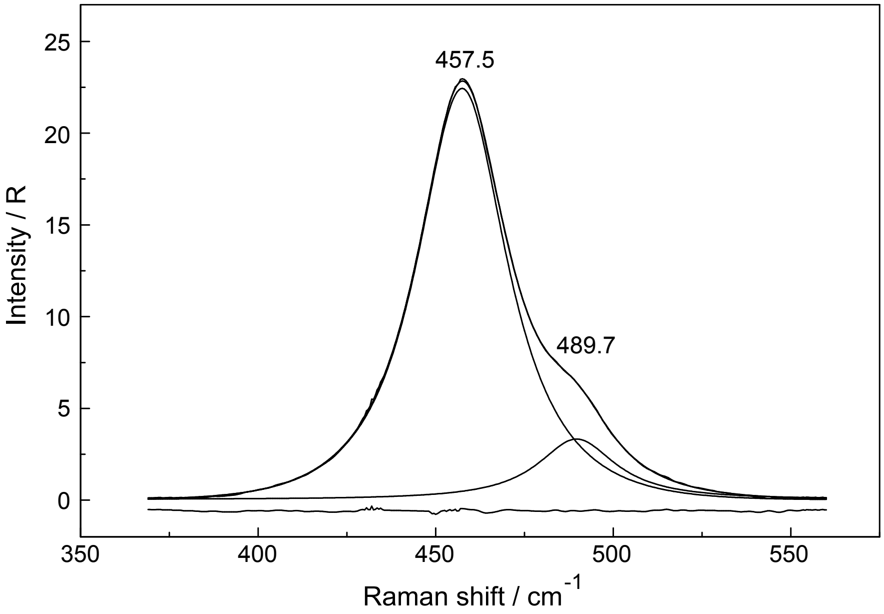

Figure S11B. Polarized Raman scattering profile in R-format (R_{VV}) of the $Ce(ClO_4)_3$ hydrate melt ($Ce(ClO_4)_3$ plus 6 H_2O) at 161°C from 370 – 575 cm^{-1}. Shown is the profile of the deformation mode, $\nu_2(e)$ ClO_4^- at 458 cm^{-1} which contains clearly two band components. Given is the measured Raman band profile, the sum curve of the band fit as well as the two band components. Underneath the band profiles, the residual curve of the fit is given (R_{VV}-profile – sum curve; $R^2 = 0.9999$).

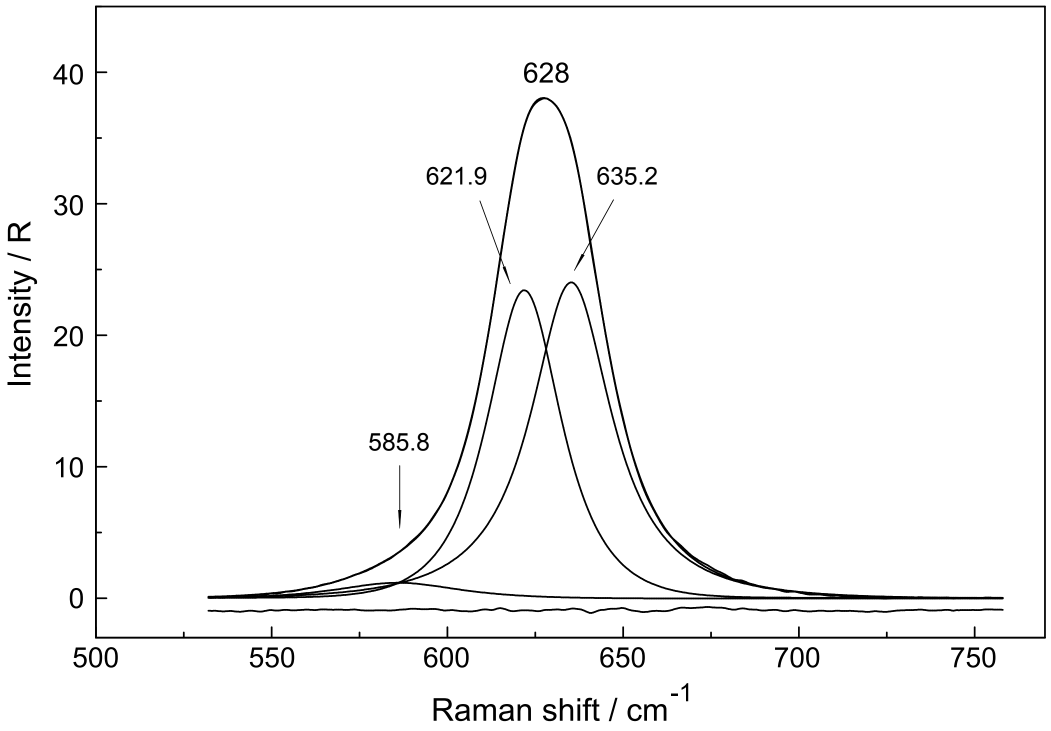

Figure S11C. Polarized Raman scattering profile in R-format (R_{VV}) of the $Ce(ClO_4)_3$ hydrate melt ($Ce(ClO_4)_3$ plus 6 H_2O) at 161°C from 530- 775 cm^{-1}. Shown is the band complex of the deformation mode, the $\nu_4(f_2)$ ClO_4^- at 628 cm^{-1}. Given is the measured Raman profile, the sum curve of the band fit as well as the three band components. Underneath the band profiles, the residual curve of the fit is given (R_{VV}-profile – sum curve; $R^2 = 0.9999$).

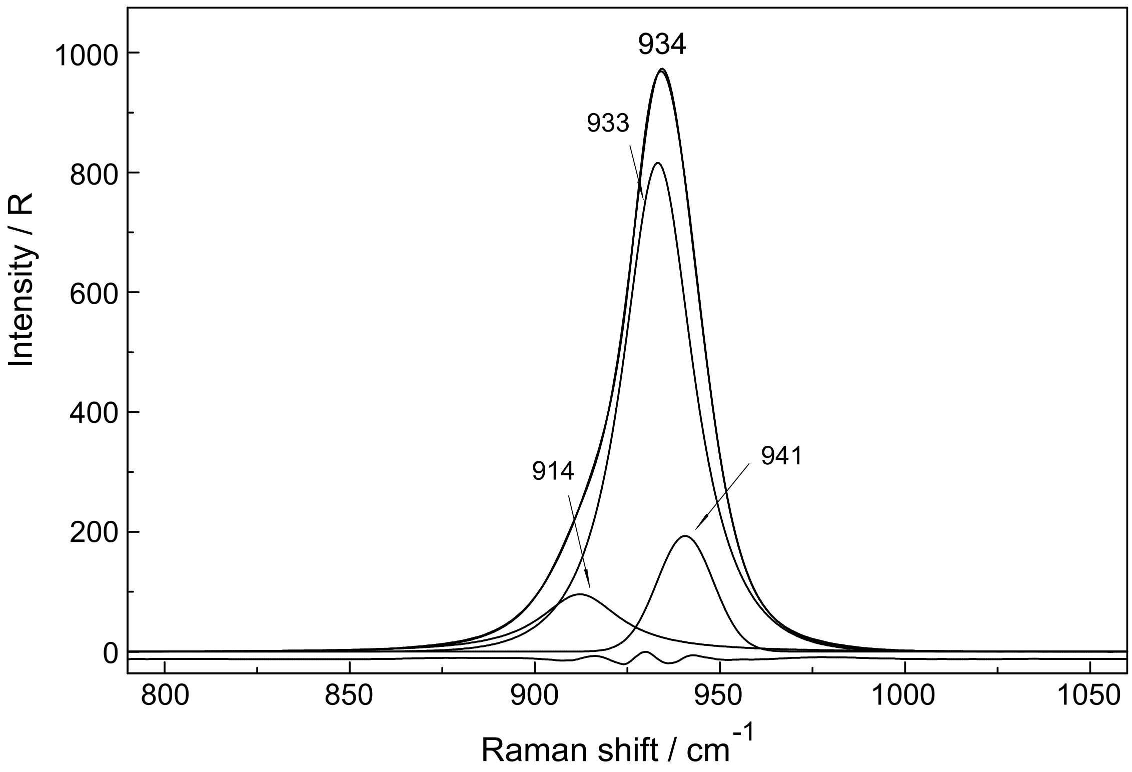

Figure S12. Isotropic Raman scattering profiles in R format (R_{iso}) of the ν_1 ClO_4^- band at 934 cm^{-1} of the $Ce(ClO_4)_3$ hydrate melt ($Ce(ClO_4)_3 + 6\ H_2O$) at 161°C. Given is the measured curve as well as the sum curve of the band. The component bands are located at 914 cm^{-1}, 933 cm^{-1} and 941 cm^{-1}. Underneath the profiles, the residual curve of the fit is given (R_{iso}-profile – sum curve; R^2 = 0.9999).

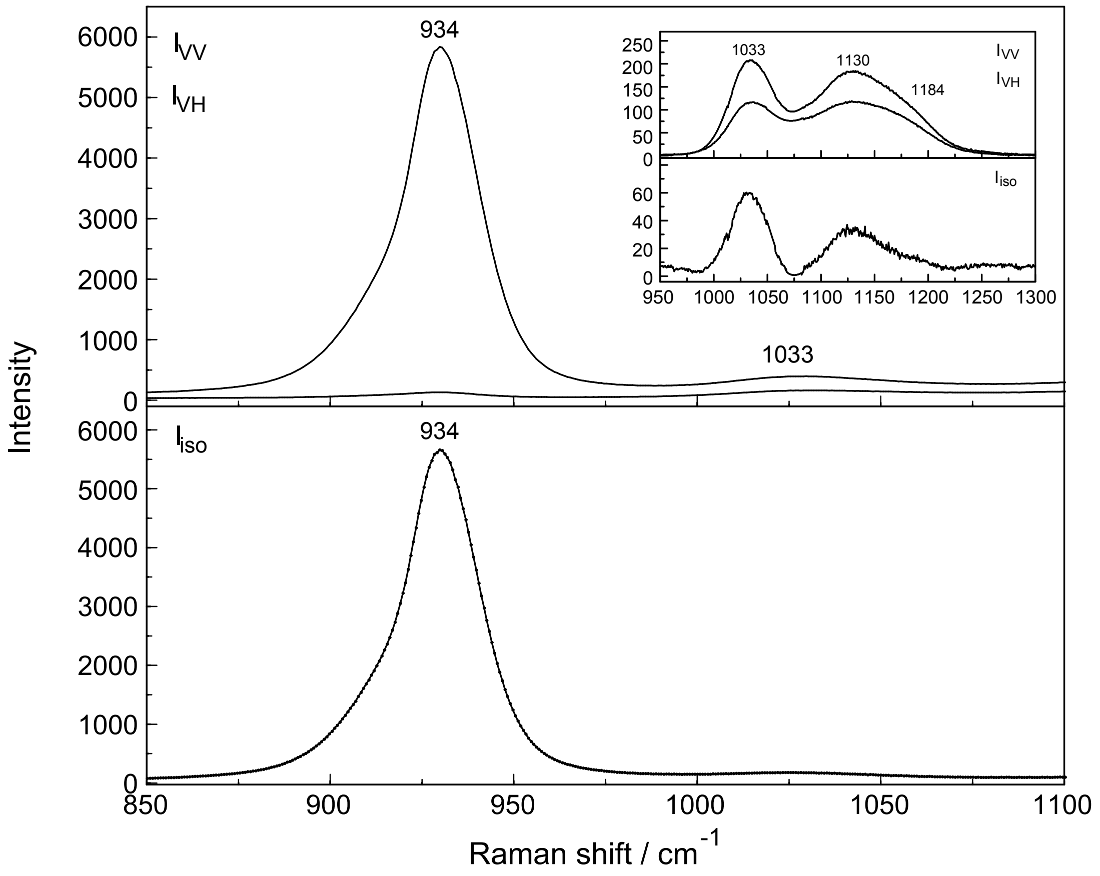

Figure S13. Raman scattering profiles of a $Ce(ClO_4)_3$ hydrate melt ($Ce(ClO_4)_3$ plus 6 H_2O) at 161°C. The upper panel depicts the I_{VV} and I_{VH} scattering profiles in the symmetric and antisymmetric stretching region (ν_1 and ν_3) region of ClO_4^-. The inset shows the weak ν_3 region of ClO_4^- in larger detail. The three components in the ν_3 region of ClO_4^- are clearly seen. The lower panel shows the isotropic scattering profile with the ν_1 ClO_4^- band region with its peak position at 934 cm^{-1} and the very weak band at 1033 cm^{-1}.