

Supplementary Information

Spectroscopic study of acetohydroxamic acid (AHA) hydrolysis in presence of europium. Implications in the extraction systems studies for lanthanides and actinides separation

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APENDIX A. Raman bands assignment

The Raman spectrum of each substance involved in the hydrolysis of AHA was separately obtained at the experiment conditions. These spectra were acquired to provide useful comparative information for assigning AHA spectrum; *i.e.* that structural features of the molecule, both backbone and functional groups, produce characteristic and reproducible vibrational bands in the spectrum. Thereby, Figure S1 shows the typical Raman spectrum under room conditions of 1) 1 mol/L AHA, 2) 0.5 mol/L acetic acid and 3) 0.5 mol/L hydroxylamine. Every aqueous solution was measured immediately after the pure components were dissolved in 0.5 mol/L HNO₃ containing 0.5 mol/L Eu(NO₃)₃. These spectra were acquired using a red laser of HeNe with a wavelength of 632.81 nm and an operation power of 20 mW from 200 to 4000 cm⁻¹ with a typical exposition time of 200 s.

Raman peaks related to the aqueous solution of HNO_3 aq. and $\text{Eu}(\text{NO}_3)_3$ aq. appear, as expected, in the three spectra and correspond to liquid water and NO_3^- nitrate ion. *i.e.* the broad band at high frequencies (2800–3400 cm^{-1}) corresponds to the OH-bond stretching, $\nu_s(\text{O-H})^1$ and the most intense band located at around 1037 cm^{-1} corresponds to the N-O stretching of the NO_3^- ion, $\nu_s(\text{NO}_3^-)^2$

Besides, the assignment of the rest of the bands shown in Figure S1 was obtained as follows. According to the assignment of hydroxylamine hydrochloride (NH_3OHCl) bands reported by Krishnan *et. al.*,³ the most intense band of this molecule (~ 1004 cm^{-1}) corresponds to the N-O stretching, $\nu_s(\text{N-O})$. The same assignment had been done for the band at ~ 912 cm^{-1} of the solid hydroxylamine by R. Nightingale and E. Wagner.⁴ Therefore, we assigned the band featured at ~ 997 cm^{-1} in this work to the N-O stretching vibration, $\nu_s(\text{N-O})$, and it was thereafter used to analyse the HA compound.

The assignment of the acetic acid Raman spectrum was performed on the basis of the results of liquid acetic acid assignment published by M. Haurie *et. al.*⁵ Hence, the main band at ~ 881 cm^{-1} was ascribed in the present work to the C-C stretching band, $\nu_s(\text{C-C})$, and it was used to analyse AcOH.

The assignment of the AHA bands was deduced by comparison with the assignment of its hydrolysis products. Thereby, we assigned the band located at ~ 950 cm^{-1} to C-C stretching (for acetic acid, $\nu_s(\text{C-C}) = 881$ cm^{-1}) and the one at ~ 985 cm^{-1} to N-O stretching (for hydroxylamine, $\nu_s(\text{N-O}) = 997$ cm^{-1}). These bands were then used to analyse the spectra of AHA.

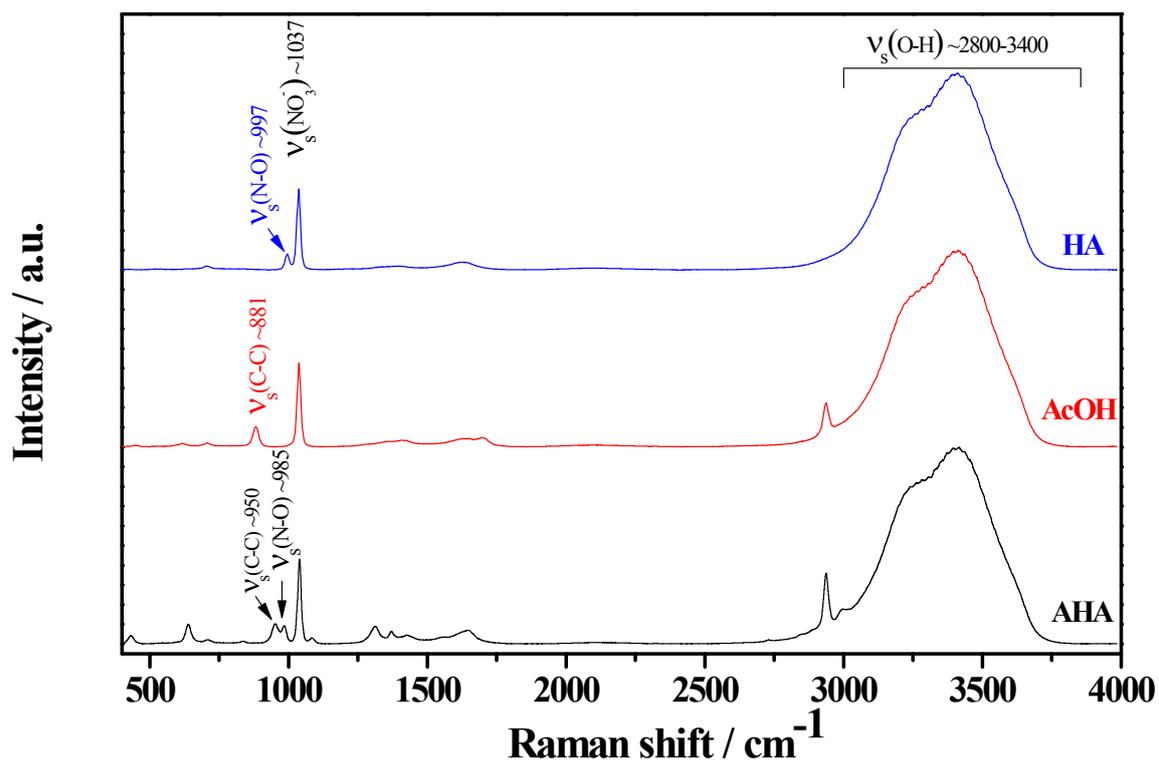


Fig S1. Raman spectra of 0.5 mol/L hydroxylamine (HA), 0.5 mol/L acetic acid (AcOH) and 1 mol/L acetohydroxamic acid (AHA) dissolved in 0.5 mol/L HNO₃ from 450 to 4000 cm⁻¹.

APENDIX B. Quantitative Raman Results (QRS)

The concentration of AHA, AcOH and HA molecules as a function of time was obtained by using quantitative Raman spectroscopy (QRS). In order to perform this quantitative analysis, different calibration curves were first obtained for the three studied molecules. For this purpose, Raman spectra of fresh AHA aqueous solutions were acquired at a concentration ranging from 0 to 1 mol/L, whereas Raman spectra of aqueous HA and AcOH were measured at a concentration from 0 to 0.5 mol/L. All solutions had been prepared with 0.5 mol/L $\text{Eu}(\text{NO}_3)_3$ at 0.5 mol/L HNO_3 . The acquired Raman spectra are shown in fig S2. These spectra were obtained at the same measurement conditions as mentioned in appendix A.

Note that all spectra were normalized to the integrated intensity of the $\nu_s(\text{NO}_3^-)$ band, since it was used as internal calibration. The integrated intensity (A) of the band was calculated from the fitting results (using a Voigt function) of the band corresponding to $\nu_s(\text{C-C})$ stretching at $\sim 950 \text{ cm}^{-1}$ for AHA, the $\nu_s(\text{C-C})$ stretching band at $\sim 881 \text{ cm}^{-1}$ for HAc, and the $\nu_s(\text{N-O})$ stretching band at $\sim 997 \text{ cm}^{-1}$ for Hydroxylamine. As an example, Fig. S3 shows the fitting performed for 1 mol/L AHA, 0.5 mol/L HA and 0.5 mol/L AcOH.

Finally, a calibration equation of linear type $C = a \cdot A + b$, where C is the molar concentration of each molecule and A is the ratio between the area of the corresponding band of each compound (A_{950} for AHA, A_{997} for HA and A_{881} for AcOH) and the band corresponding to NO_3 (A_{1037}), was obtained for all the species (see Fig. S4).

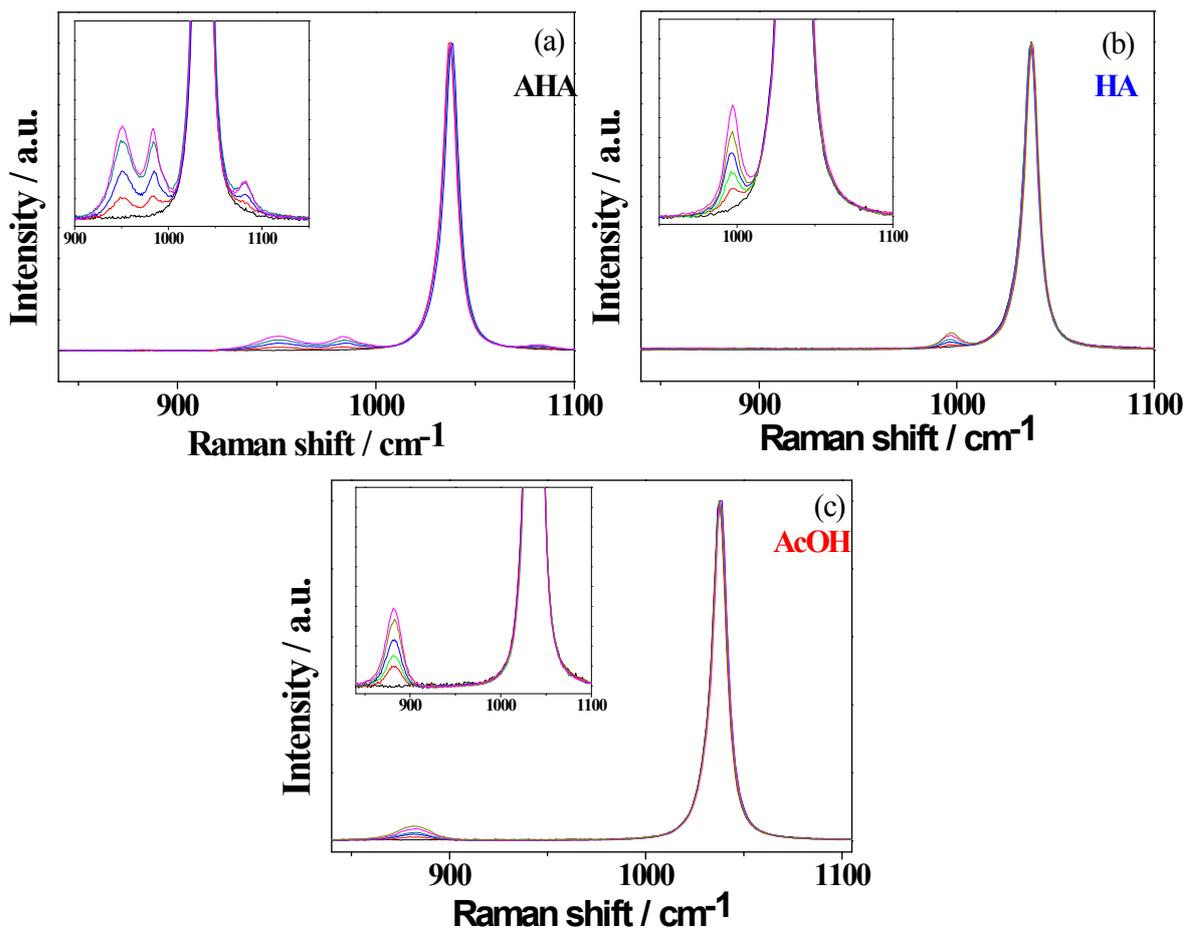


Fig. S2. Experimental Raman spectra of aqueous solutions of $0.5 \text{ mol/L Eu}(\text{NO}_3)_3$ at 0.5 mol/L HNO_3 with (a) AHA fresh from 0 mol/L to 1 mol/L , b) HA from 0 mol/L to 0.5 mol/L , and c) AcOH from 0 mol/L to 0.5 mol/L .

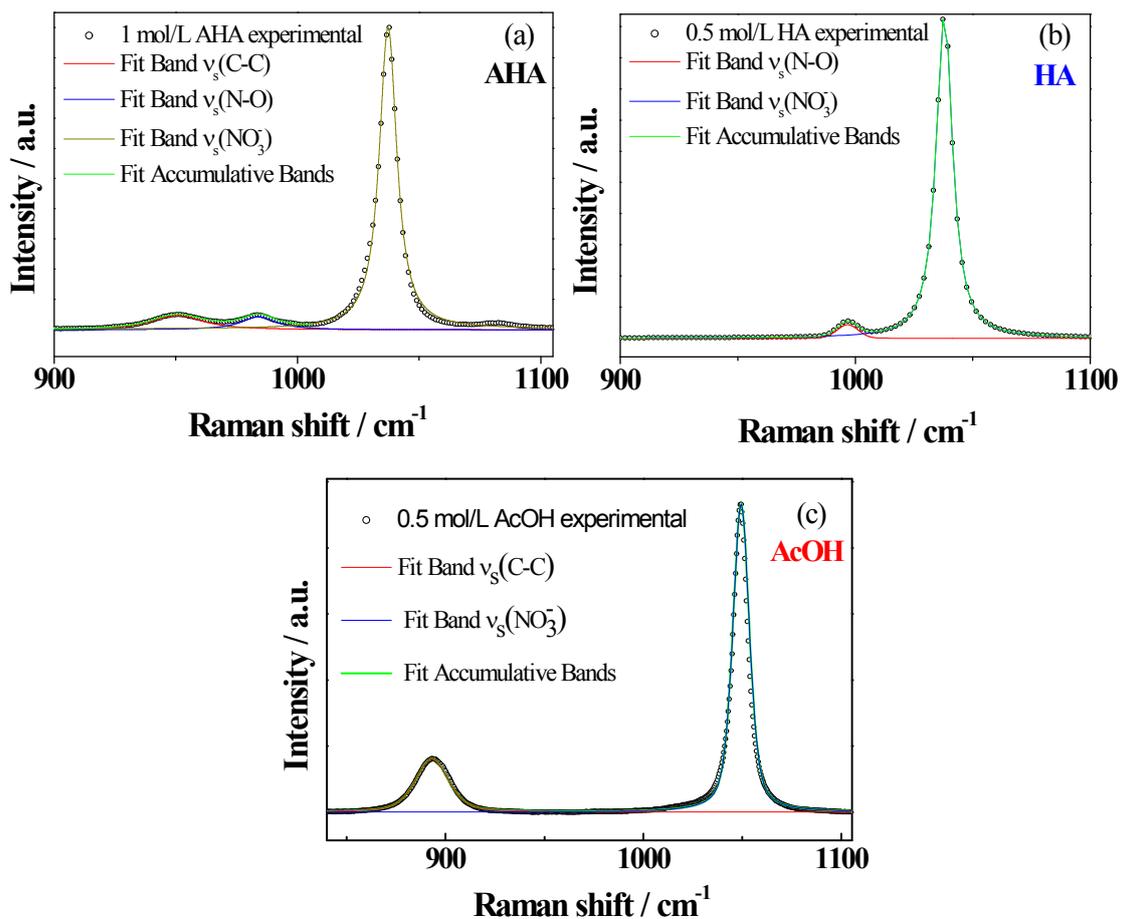
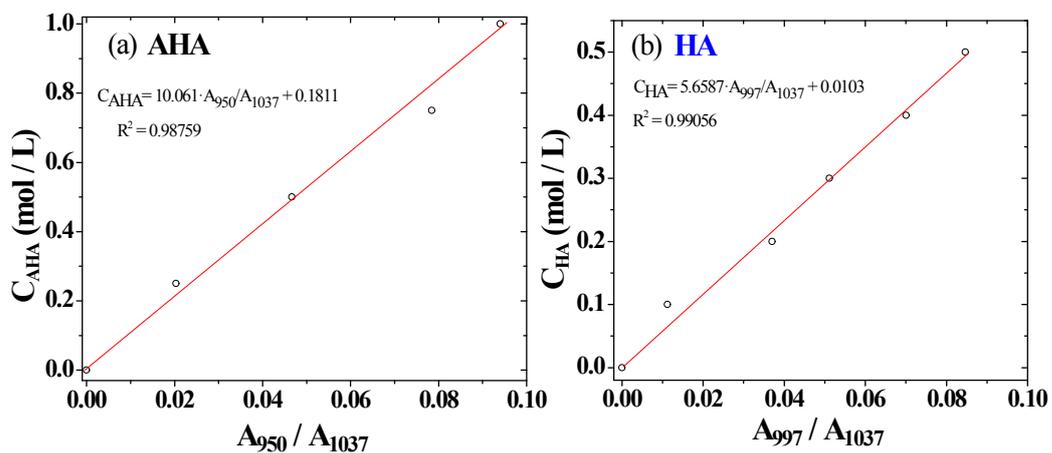


Fig. S3. Fitted Raman spectra for main bands of 0.5 mol/L $\text{Eu}(\text{NO}_3)_3$ at 0.5 mol/L HNO_3 with (a) 1 mol/L AHA fresh, b) 0.5 mol/L HA, and c) 0.5 mol/L AcOH.



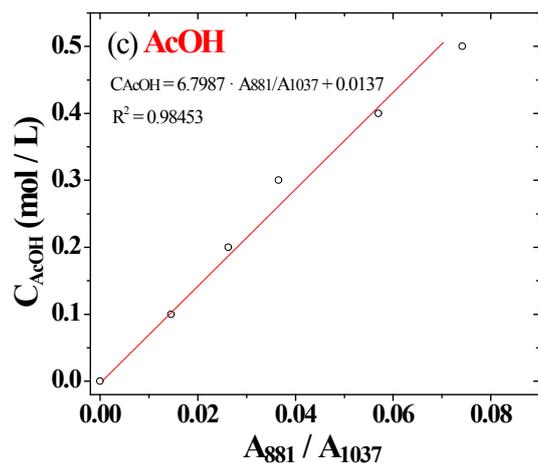


Fig. S4. Calibration curves of 0.5 mol/L $\text{Eu}(\text{NO}_3)_3$ at 0.5 mol/L HNO_3 with different concentrations of (a) AHA, (b) HA and (c) AcOH.

References

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