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Isotopic effect on the formation kinetics of Pu(IV) intrinsic colloids

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Fundamental knowledge of the intrinsic colloids of plutonium is a major issue in predicting their behavior in the environment.[1,2] It has been demonstrated that these species are spherical nanoparticles measuring *ca.* 2 nm with a local structure similar to the one of bulk PuO₂. [3,4] Recent studies have questioned the contribution of small Pu clusters in the formation mechanism of Pu(IV) intrinsic colloids.[5] The current work draws attention to this issue by investigating an unprecedented kinetic isotopic effect (KIE) observed during the preparation of Pu(IV) colloids in light (H₂O) or heavy (D₂O) water.

Plutonium colloids have been synthesized by the dilution of acidic Pu(IV) solutions in H₂O and D₂O. Time dependent measurements carried out with UV-Vis absorption spectroscopy demonstrated a much lower formation rate of the Pu(IV) colloids in D₂O compared to H₂O (Figure 1a). The observed KIE was attributed to the difference in zero-point energies of O-H and O-D bonds. This finding has confirmed that the formation of Pu(IV) colloids is limited by the rupture of O-H bonds during hydrolysis and polymerization of Pu(IV) species. In addition, formation of some unstable intermediate Pu(IV) species was observed during colloid formation. A thorough investigation of this intermediate using synchrotron SAXS and XAS techniques revealed the presence of an hexanuclear Pu(IV) cluster of quasi-spherical shape measuring *ca.* 0.8 nm and agreeing with the literature (Figure 1b).[6,7]

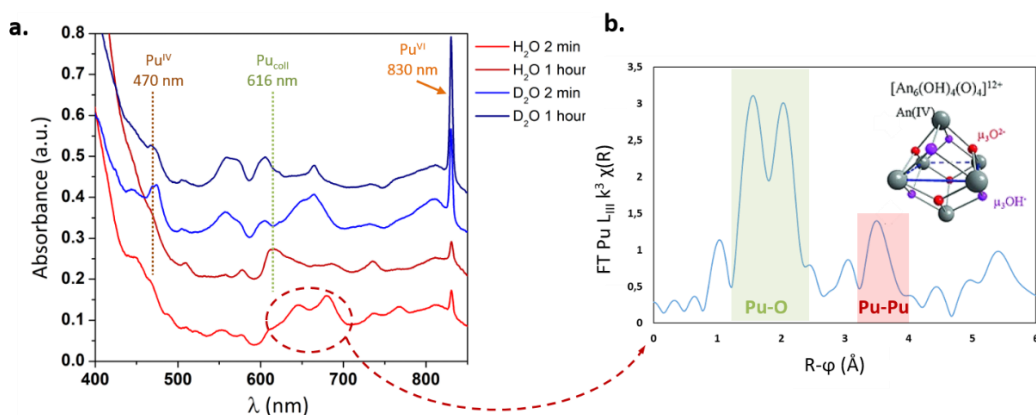


Figure 1: (a) UV-Vis absorption spectra acquired during the synthesis of 5 mM Pu(IV) hydrolytic colloids in H₂O (red lines) and D₂O (blue lines). (b) k^3 -weighted Fourier transform (FT) of the intermediate species observed in H₂O by UV-Vis absorption spectroscopy (dashed circle).[6]

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