

SUPPORTING INFORMATION

Insights into the solution structure of the hydrated uranyl ion from neutron scattering and
EXAFS experiments

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Experimental Section

Uranyl chloride was prepared by repeated dissolution and evaporation of uranyl nitrate and HCl followed by slow evaporation of a concentrated solution to form a crystalline mass. Purity was checked by single crystal XRD¹ and IR spectroscopy. Neutron scattering data were collected at the Small Angle Neutron Diffractometer for Amorphous and Liquid Samples (SANDALS) at the ISIS pulsed neutron source of the Rutherford Appleton Laboratory, UK. 1.5 cm³ of three isotopically distinct but otherwise identical samples were prepared by dissolving an appropriate amount of uranyl chloride in H₂O, D₂O (Sigma-Aldrich 99.9 atom % D), and a 1:1 H₂O:D₂O mixture to give a 1.0M solution; the resultant pH was ~3. For the neutron scattering measurements, each of the solutions was transferred to null scattering Ti_{0.676}Zr_{0.324} alloy cells, where the cell walls of 1 mm thickness define an internal sample volume of dimensions 1 mm thickness x 35 mm width x 40 mm height. The filled cells were loaded onto the instrument's automatic sample changer, and the temperature of each sample was controlled to be 25±0.1 °C.

After collection, the experimental data were corrected for background scattering, absorption, and multiple scattering and normalized to the scattering from a vanadium standard using the Gudrun routines that are based on the algorithms of the widely used ATLAS package.² The resulting functions were corrected for the self- and inelastic scattering contributions following the methods of Soper and Luzar,³ and the interference differential scattering cross sections $F(Q)$ shown in Figure S1 are obtained.

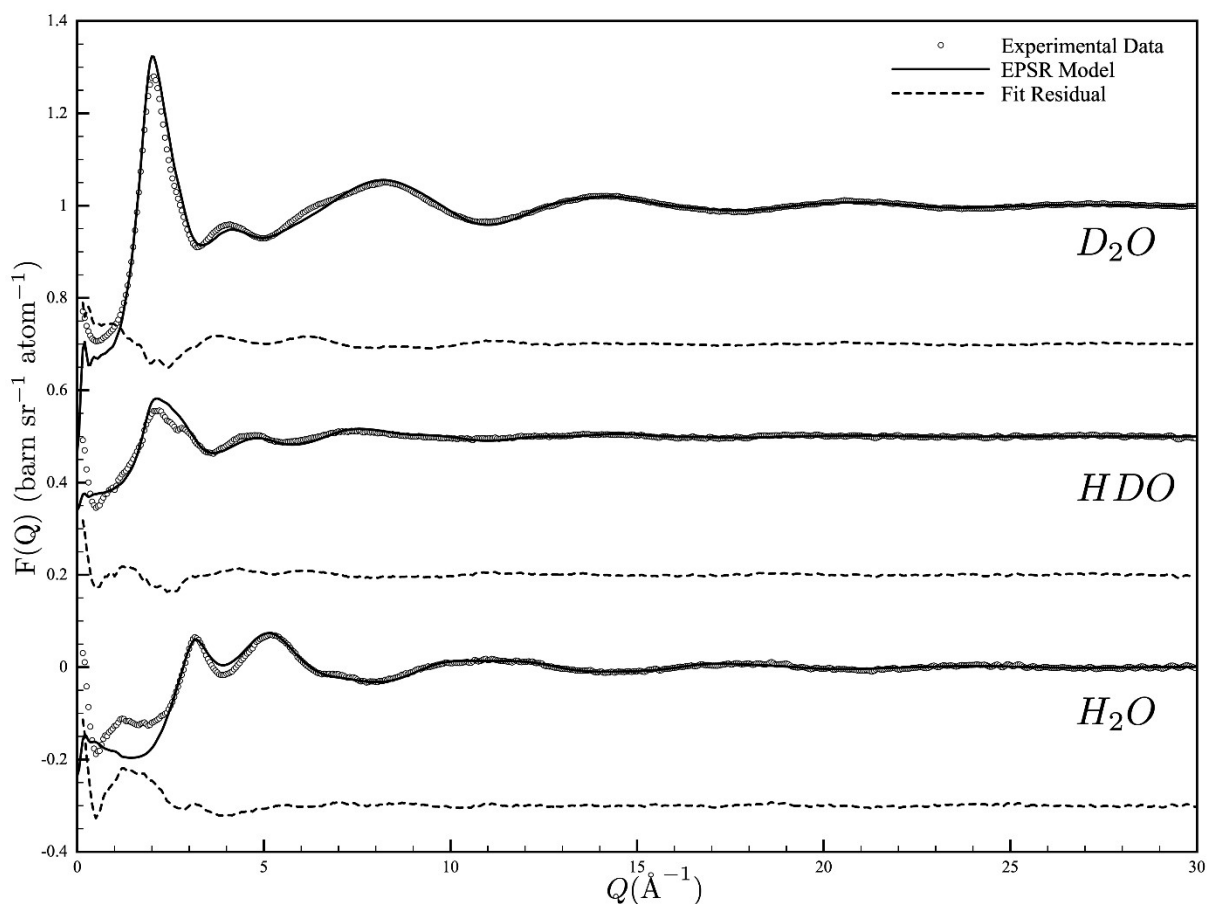


Fig S1.

Once the EPSR model has been refined, the simulation is continued, and snapshots of the local environments around the uranyl ions, to a radius of 10 Å, are periodically extracted. These are then input into an EXAFS signal calculation (FEFF8)⁴ and the results ensemble averaged.⁵

It is important to note that although the EXAFS information is not directly used to drive the structure refinement, it provides a stringent test of how effectively the cation is incorporated into the bulk structural model. Comparison of the fit to the experimental data⁶ (Fig S2) shows numerous discrepancies in both amplitude and especially the peaks at $k \sim 7-9 \text{ \AA}^{-1}$ in the EXAFS data. Structural data extracted from this model are shown in Fig S3.

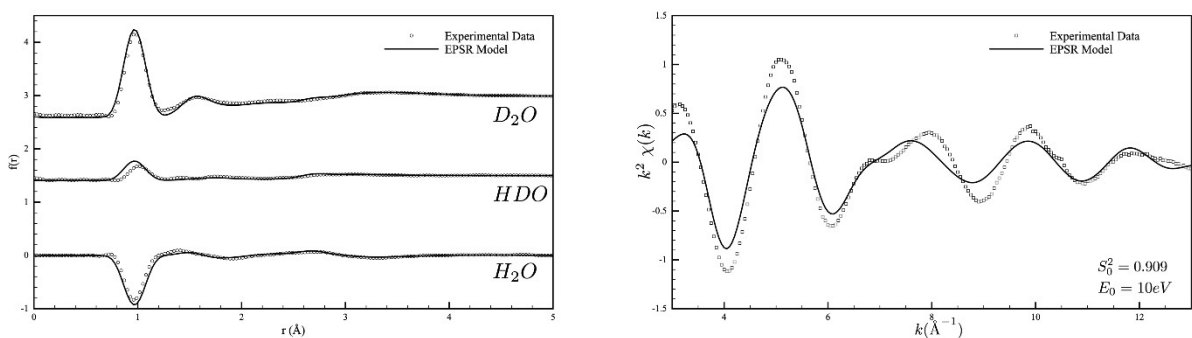


Fig S2.

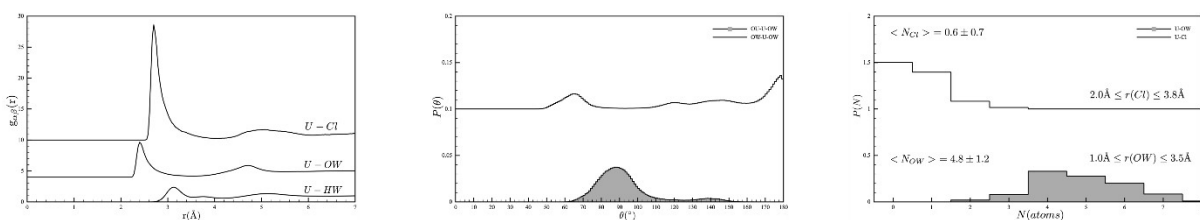


Fig S3. Partial Pair Distribution functions (left), water angular data (middle) and coordination environment of the uranyl ion (left) from the free model.

The poor fit and the broad spread of water angles led us to constrain two of the water molecules as shown in Fig S4, and the fit to the experimental data more satisfactory, as shown in Fig S5. Additional data extracted from this model are given in Figs S6-S8.

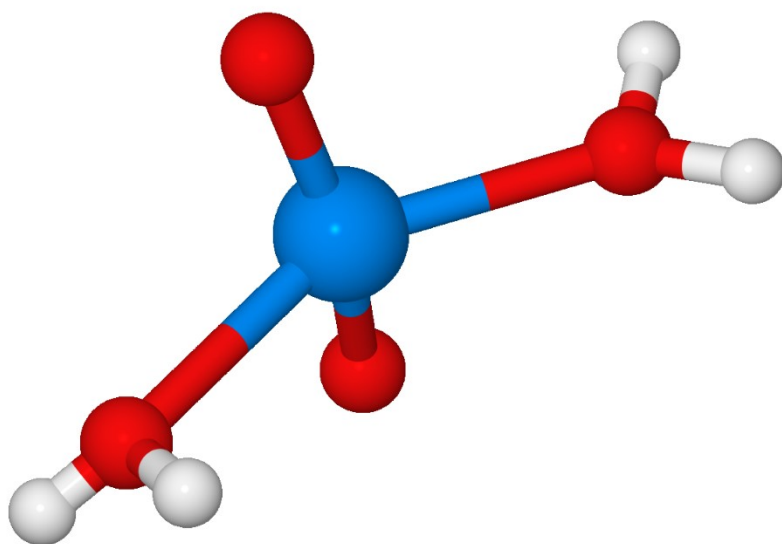


Fig S4. Constrained water coordination on the model

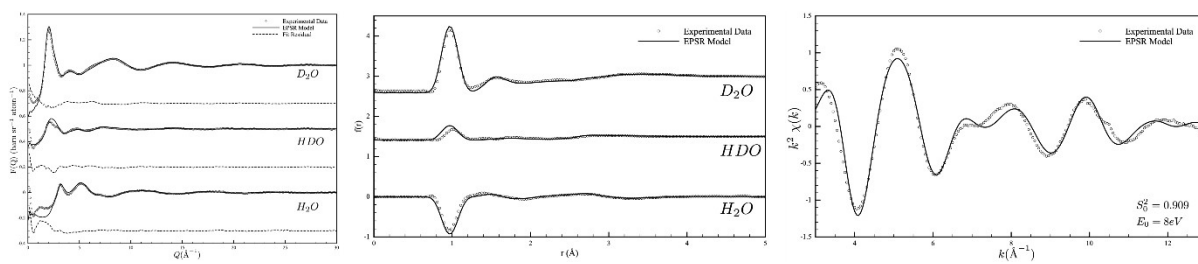


Fig S5. Data from the constrained model.

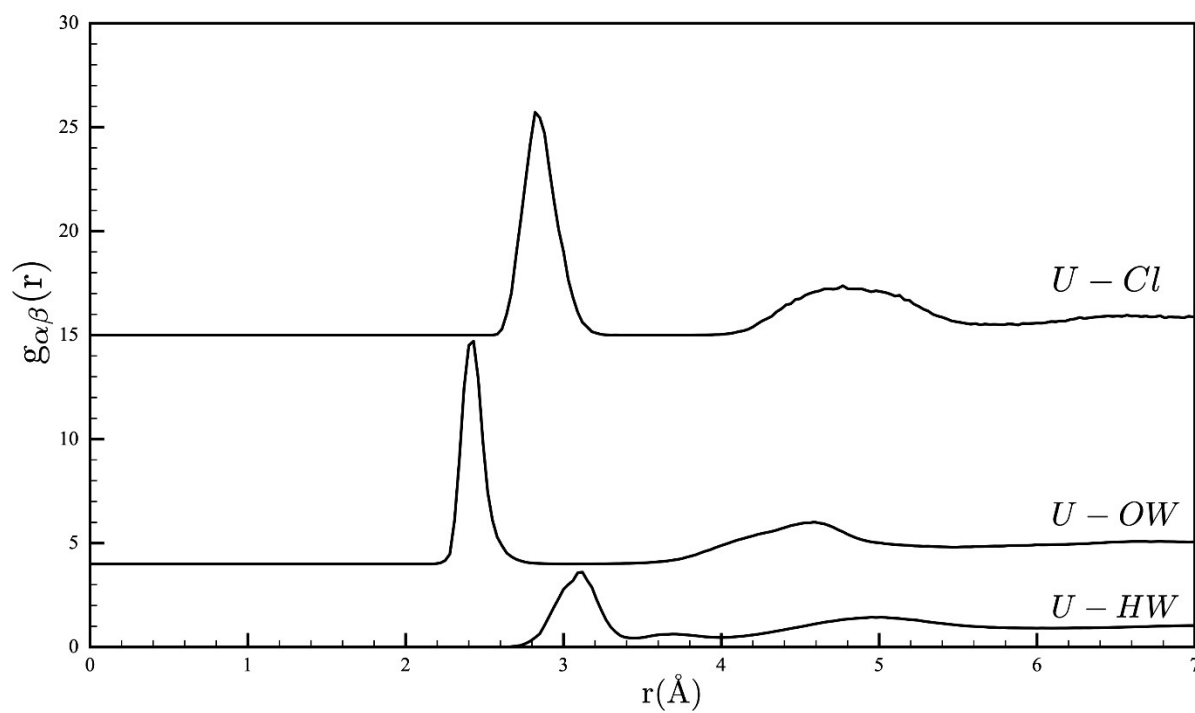


Fig S6. Uranium centred partial distribution functions to OW, HW and Cl.

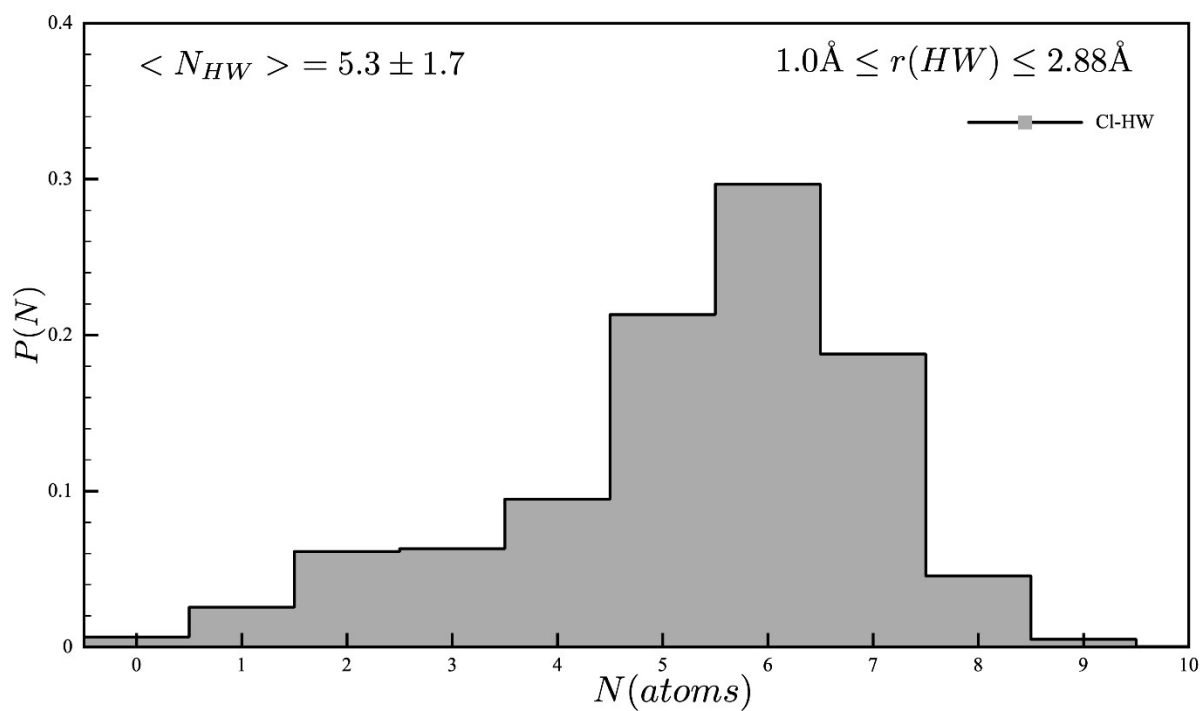


Fig S7. Chloride hydration sphere from the constrained fit.

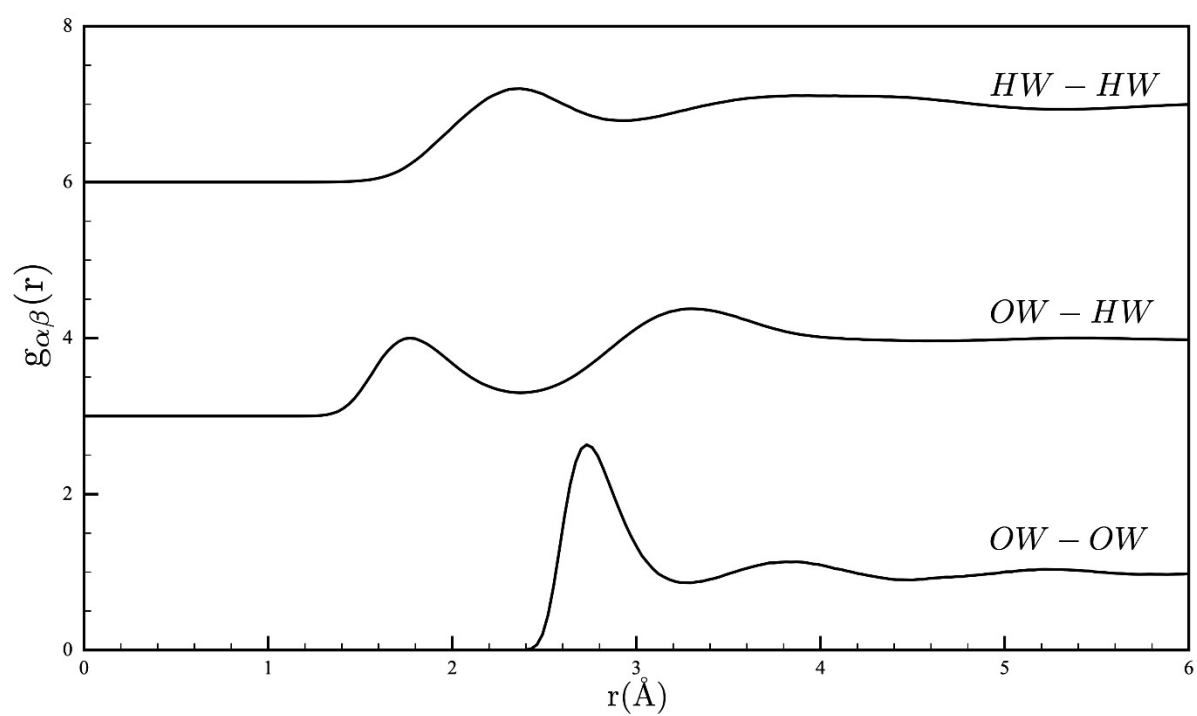


Fig S8. Partial pair distribution functions of the bulk water, from the constrained fit.

References

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