

# Solvation of $\text{Au}^+$ versus $\text{Au}^0$ in aqueous solution: electronic structure governs solvation shell patterns

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The solvation behavior of  $\text{Au}^+$  and  $\text{Au}^0$  in liquid water under ambient conditions has been studied using *ab initio* molecular dynamics. The  $\text{Au}^+$  aqua ion forms a rigid and well-defined quasi-linear structure in the sense of ligand field theory, where two water molecules are tightly bound to the gold cation through oxygen atoms (“cationic solvation”). Yet, transient charge accumulation in the direction perpendicular to the  $\text{O}-\text{Au}^+-\text{O}$  linear core structure leads occasionally to the formation of a short  $\text{Au}^+-\text{H}$  contact within the distance range of the first solvation shell, which is typical of “anionic solvation”. Upon adding an electron to  $\text{Au}^+$ , the resulting solvation pattern of  $\text{Au}^0(\text{aq})$  has nothing in common with that of  $\text{Au}^+(\text{aq})$ . Quite surprisingly we discover that the first solvation shell of  $\text{Au}^0(\text{aq})$  consists of a single water molecule and features both “anionic” and “cationic” solvation patterns depending on fluctuation and polarization effects. Thus, charging/decharging of metals dissolved in water,  $\text{M}^0 \leftrightarrow \text{M}^+ + \text{e}^-$ , as occurring *e.g.* during elementary electrochemical steps, is expected to change dramatically their solvation behavior in the sense of re-solvation processes.