Solvation of Au$^+$ versus Au$^0$ in aqueous solution: electronic structure governs solvation shell patterns

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The solvation behavior of Au$^+$ and Au$^0$ in liquid water under ambient conditions has been studied using ab initio molecular dynamics. The 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 O–Au$^+$–O linear core structure leads occasionally to the formation of a short Au$^+$–H contact within the distance range of the first solvation shell, which is typical of “anionic solvation”. Upon adding an electron to Au$^+$, the resulting solvation pattern of Au$^0$(aq) has nothing in common with that of Au$^+$ (aq). Quite surprisingly we discover that the first solvation shell of Au$^0$(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, M$^0 \leftrightarrow M^+ + e^-$, as occurring e.g. during elementary electrochemical steps, is expected to change dramatically their solvation behavior in the sense of re-solvation processes.

I. Motivation

Metal ions in water continue to receive considerable attention due to their fundamental importance not only in chemistry and industry but also in medicine and toxicology to name but a few prominent fields. They play important roles in living systems: some heavy metal ions such as Hg$^{2+}$ and Cd$^{2+}$ are highly toxic to organisms, whereas the Ca$^{2+}$ ion is ubiquitous in biological systems, performing a variety of roles including functioning as a second messenger in numerous processes such as cell division and growth, ion transport and muscle contraction. Gold, in particular, has been successfully used in the therapy for rheumatoid arthritis in rats, while gold promoted oxides in contact with aqueous solutions are employed in heterogeneous catalysis. Here, both neutral and cationic gold species are relevant and thus their solvation behavior in water is of immediate interest to broad communities.

Over the last few decades, a wide range of experiments and computer simulations have been performed to investigate the structure and dynamics of solvated metal ions, whereas far less is known about the solvation of their neutral counterparts. However, converting cationic into neutral species, and vice versa, plays a key role in a wide variety of chemical and biological processes or in liquid-phase heterogeneous catalysis and electrochemistry to name but a few.

Since the first ab initio simulation of the solvation of a metal cation in water, Be$^{2+}$(aq), ab initio molecular dynamics has been used widely to study the solvation behavior of ions in water. Transition metal cations turn out to be particularly rich in their solvation behavior: this is because pronounced electronic structure effects—first-shell H$_2$O molecules being ligands in the sense of inorganic coordination complexes—compete with typical liquid-state packing and (di)polar ordering effects.

Recently ab initio molecular dynamics has been successfully employed to investigate the hydration of various transition metal cations, Cu$^{2+}$, Ag$^{+}$, Pt$^{2+}$, Cu$^{2+}$, Cr$^{3+}$, or Y$^{3+}$, as well as that of lanthanides, Gd$^{3+}$ or La$^{3+}$. Ab initio computer simulations indicate that the Cu$^{2+}$ aqua ion has a low coordination number of two with a variable number of water molecules at larger distances, whereas Ag$^{+}$ prefers coordination by four approximately equivalent water molecules. Interestingly, the Cu$^{2+}$ aqua ion features a typical “anionic” solvation pattern: the accumulation of negative charge protruding sideways perpendicular to the axis of the Cu$^{2+}$ dihydrate leads occasionally to short Cu$^{2+}$–H contacts. A similar anionic arrangement has been recently observed in the Pt$^{2+}$ aqua ion. At variance with Cu$^{2+}$(aq), the Pt$^{2+}$ aqua ion exhibits a well-defined square-planar first solvation shell encompassing four tightly bonded water molecules as expected from simple ligand field theory arguments, and an anisotropically structured second coordination shell. Additional solvation in the axial regions,

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