The elusive coordination of the Ag^+ ion in aqueous solution: evidence for a linear structure

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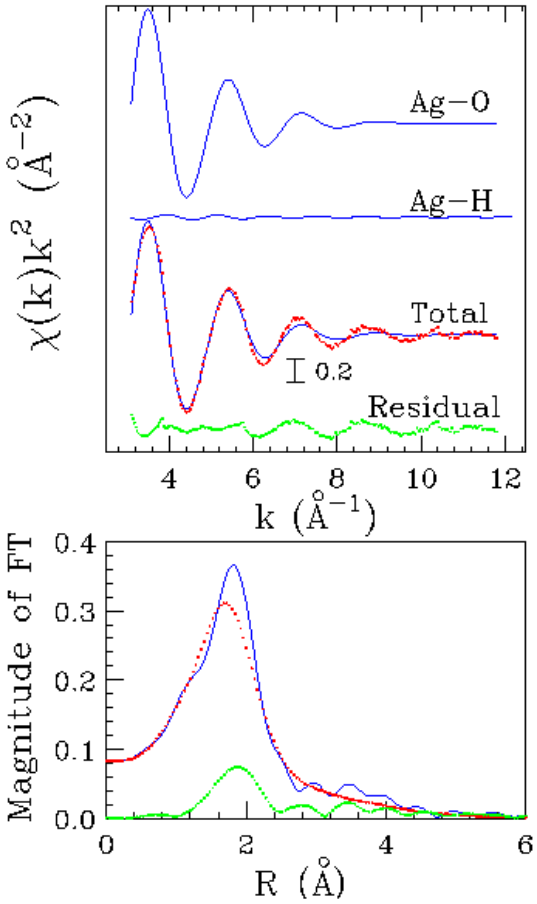

Figure S1: Upper panel: analysis of the Ag K-edge EXAFS spectrum of the 0.2 mol·dm^{-3} $AgClO_4$ aqueous solution with CN=4. From the top the best fit theoretical Ag-O and Ag-H two-body contributions are shown, as well as the total theoretical signal (blue line) together with the experimental spectrum (red dots) and the corresponding residuals (green line). Lower panel: non-phase shift corrected Fourier Transforms of the best-fit EXAFS theoretical signal (blue line) of the experimental data (red dots) and of the residual curve (green line).

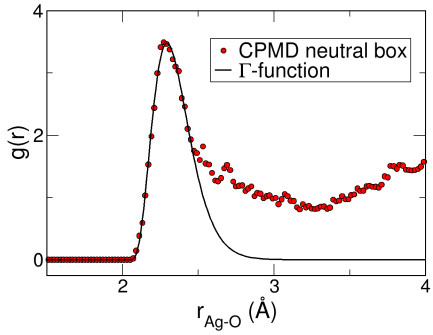

Figure S2: Ag-O radial distribution function *g(r)* obtained from the CPMD simulation of the neutral system (red dots) and corresponding Γ-like function obtained from the fitting procedure up to an Ag-O distance of 2.5 Å (black line).

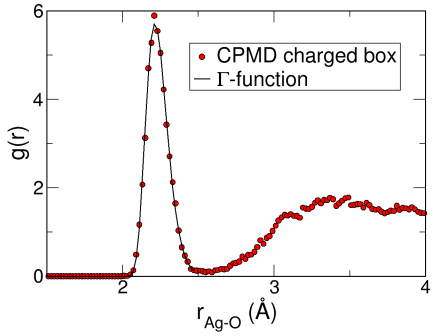

Figure S3: Ag-O radial distribution function *g(r)* obtained from the CPMD simulation of the positively charged system (red dots) and corresponding Γ-like function obtained from the fitting procedure up to an Ag-O distance of 2.5 Å (black line).

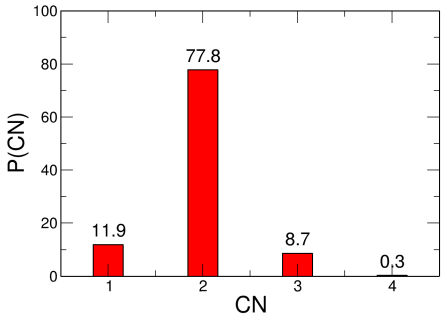

Figure S4: Instantaneous Ag-O coordination number (CN) distribution, expressed in percentage, obtained from the CPMD simulation of the neutral system up to a cutoff Ag-O distance of 2.5 Å.

Table S1: Details about literature crystal structures of Ag^+ aquo-complexes involving 2 - 4 water molecules.

Coordination	Database Identifier	Ag-O bond distance (Å)	References
2-fold	RUKZUT	2.112	[1]
	DELVAR	2.125	[2]
	UFAGEO, UFAGEO01	2.135	[3,4]
	YUCMIT	2.137	[5]
		Mean bond: 2.128 Å	
2/4-fold	432327	2.271 + 2.620 (2F)	[6]
	RUDPOW	2.248 (ca. 3.2 Å)	[7]
4-fold	DAGCOG	2.432	[8]
	HAQNIY	2.395	[9]
	74965	2.469	[10]

Table S2: Coordination number CN, first maximum position R_{max}, first peak average value R, Debye-Waller factor σ^2 and peak asymmetry β of the CPMD Ag-O *g(r)* as obtained by modeling the first peak with a Γ-like function.

CN	R_{max} (Å)	R (Å)	σ^2 (Å^2)	β
2.0	2.21	2.24	0.006	0.6

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