Table SI-1. Optimised structures (distances in Å and angles in degrees), hydration energies of the first solvation shell, ΔE, and successive water binding energies, ΔE_{inc}, (in kcal mol^{-1}) of the $Mg(H_2O)_n^{2+}$ clusters computed using the PBE/US-PW and PBE/DNP methods [a)]. $\Delta E = E[Mg(H_2O)_n^{2+}] - E[Mg^{2+}] - nE[H_2O]$; $\Delta E_{inc} = E[Mg(H_2O)_{n+1}^{2+}] - E[Mg(H_2O)_n^{2+}] - E[H_2O]$. In all PWSCF calculations, cutoffs for the smooth part of the wavefunctions and the augmented density were set to 30 and 200 Ry.

	***r*(Mg–O)**		***r*(O–H)**		**θ(H–O–H)**		**ΔE**		**ΔE_{inc}**	
	DNP	**PW**	**DNP**	**PW**	**DNP**	**PW**	**DNP**	**PW**	**DNP**	**PW**
H_2O			0.97	0.99	104.0	104.5				
$Mg(H_2O)^{2+}$	1.94	1.92	0.99	1.00	105.7	106.1	-81.7	-85.3	-81.7	-85.3
$Mg(H_2O)_2^{2+}$	1.96	1.94	0.99	1.00	105.5	106.1	-153.6	-158.5	-72.0	-73.2
$Mg(H_2O)_3^{2+}$	1.99	1.98	0.98	1.00	105.4	105.8	-212.4	-217.3	-58.7	-58.8
$Mg(H_2O)_4^{2+}$	2.02	2.01	0.98	0.99	105.4	105.7	-259.8	-263.6	-47.4	-46.3
$Mg(H_2O)_5^{2+}$	2.07	2.07	0.98	0.99	105.7	106.3	-291.9	-294.1	-32.1	-30.5
$Mg(H_2O)_6^{2+}$	2.11	2.11	0.98	0.99	106.1	106.4	-321.1	-321.9	-29.2	-27.8

[a)] All-electron calculation using the $DMol^3$ code (Delley, B. J. Chem. Phys. 1990, 92, 508; Delley, B. J. Chem. Phys. 2000, 113, 7756), the PBE density functional and the double-numeric-polarised (DNP) basis sets on all atoms method.

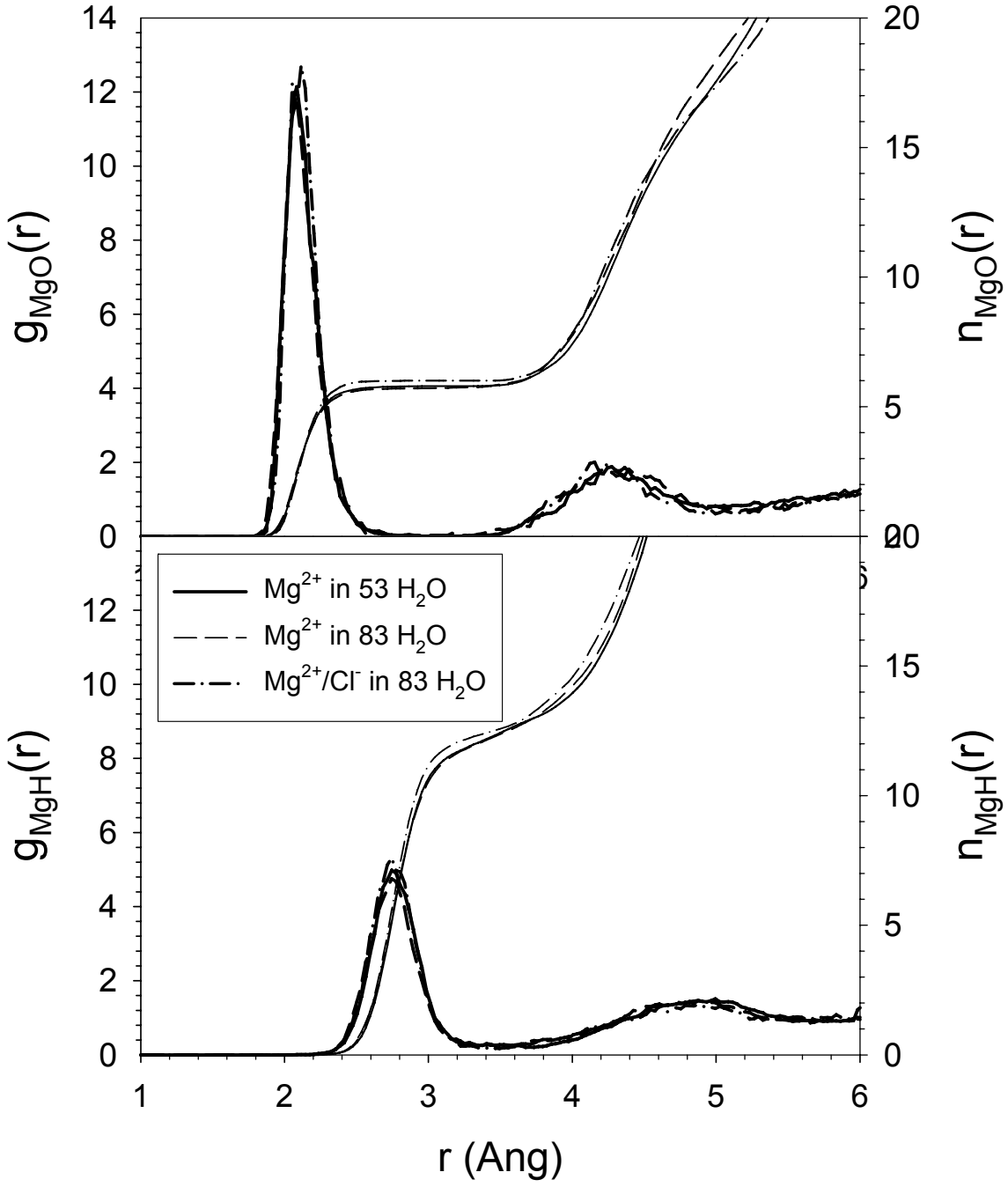

Figure SI.1. Mg−O and Mg−H radial distribution functions, $g(r)$, and running coordination number, $n(r)$, obtained from the CP-MD simulations of Mg^{2+} in 53 H_2O, Mg^{2+} in 83 H_2O and Mg^{2+}/Cl^- in 82 H_2O.

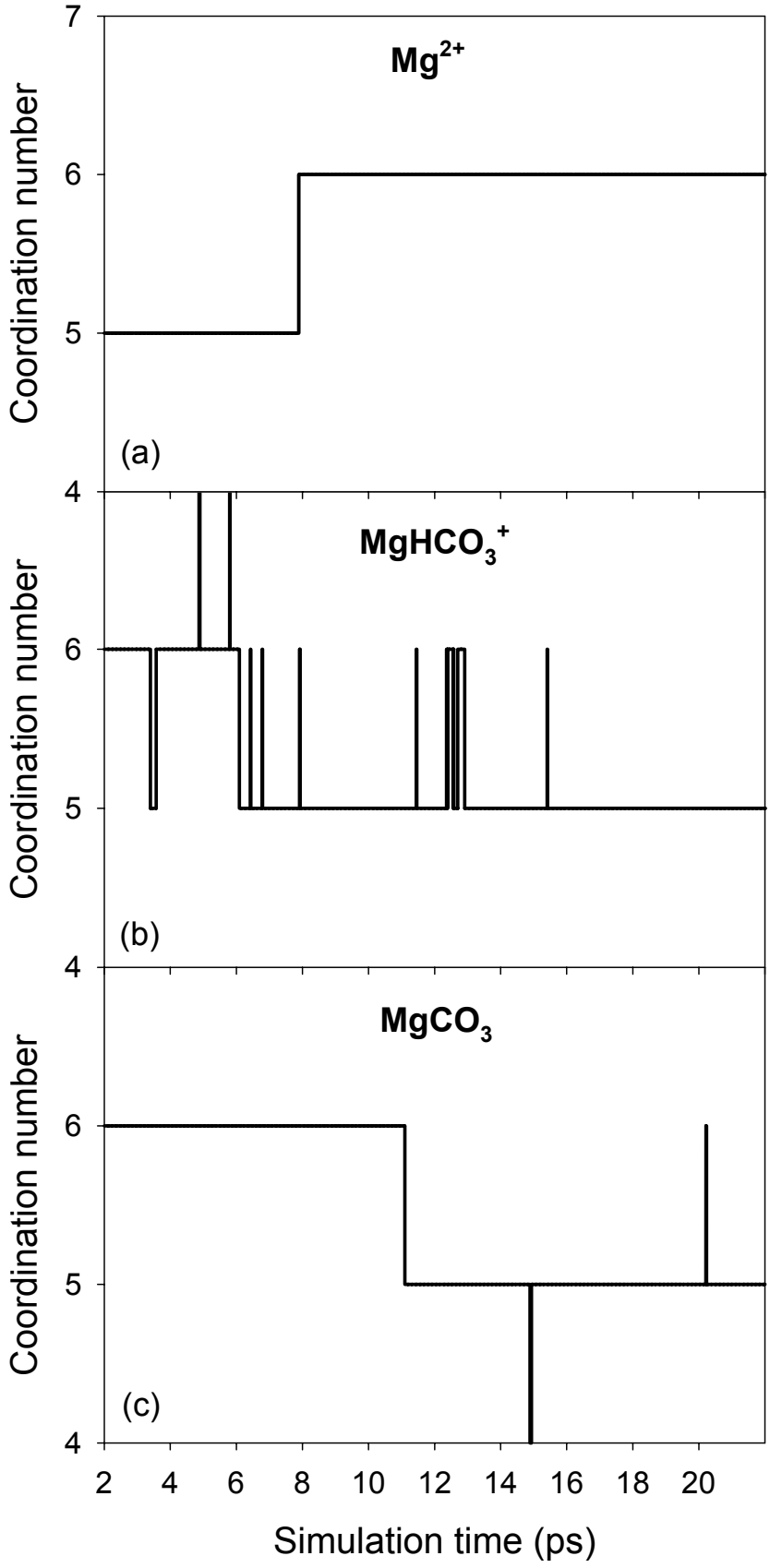

Figure SI.2. Time dependence of the first-shell coordination number of the magnesium atom obtained from the CP-MD simulations of (a) Mg^{2+}, (b) $MgHCO_3^+$ and (c) $MgCO_3$ in water.

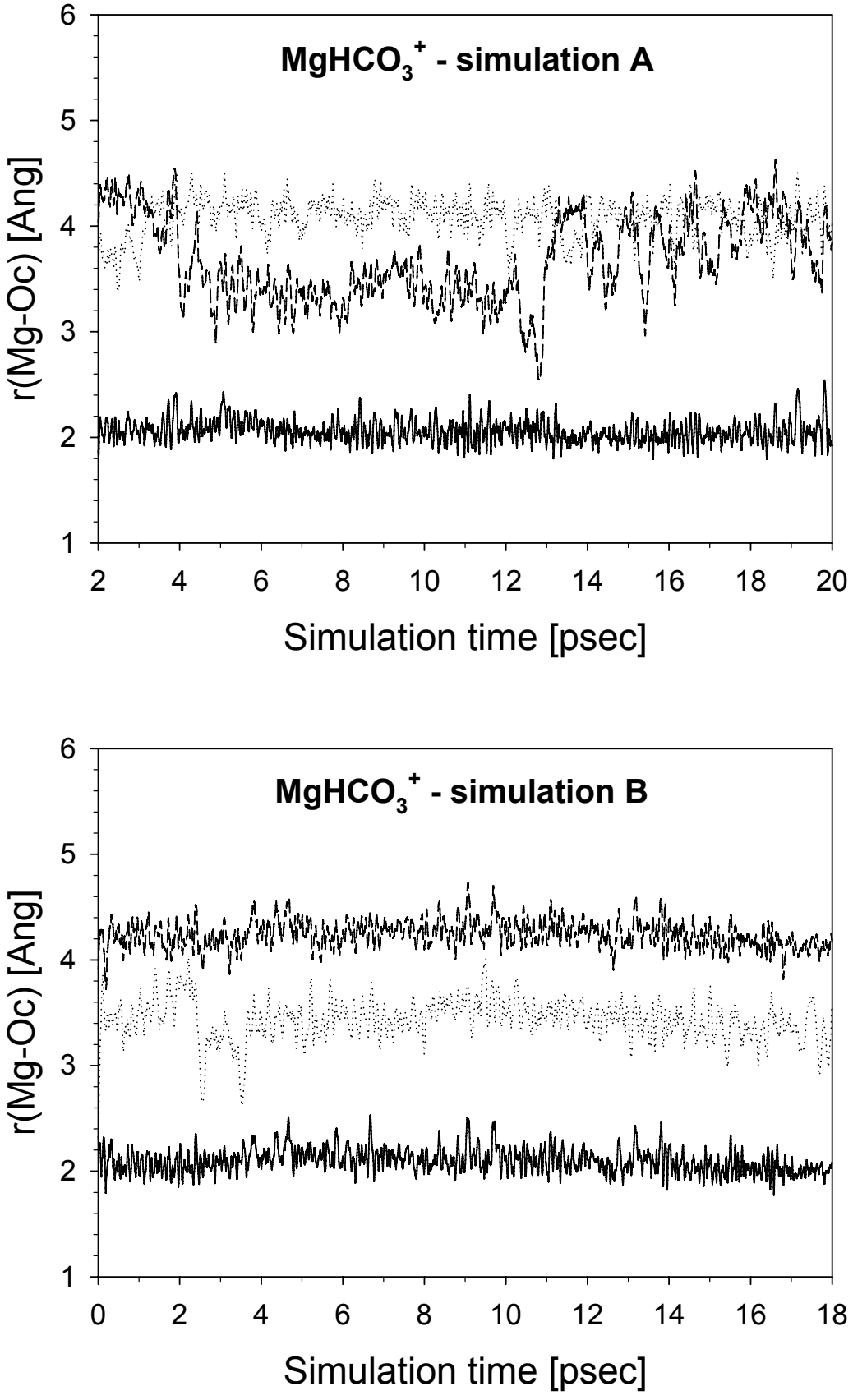

Figure SI.3. Time evolution of Mg–O distances for the oxygen atoms of the bi-carbonate ion. In Simulation **A** the initial coordination of HCO_3^- to the magnesium

was mono-dentate (η^1); in simulation **B** the initial coordination of HCO_3^- to the magnesium was bi-dentate (η^2).

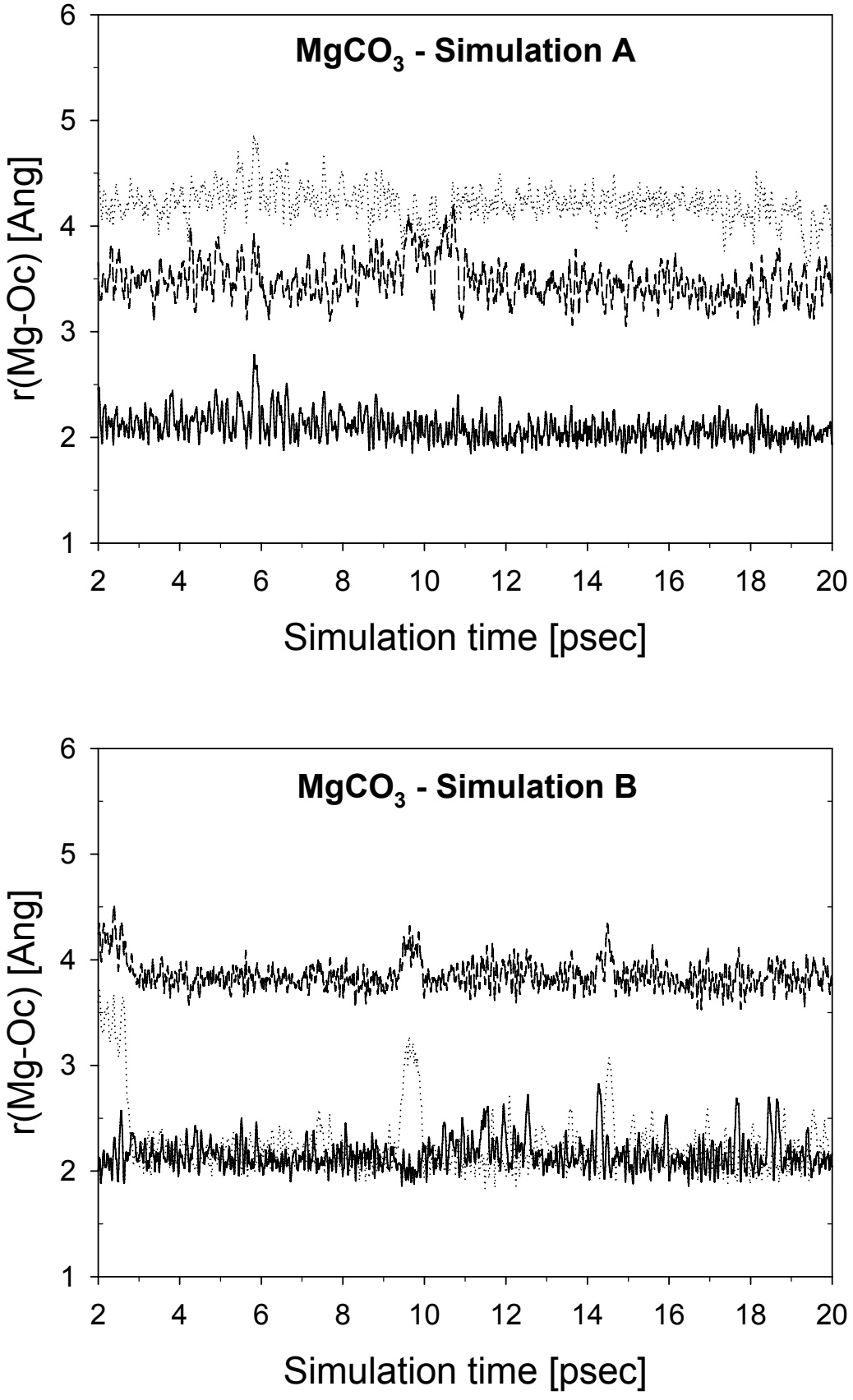

Figure SI.4. Time evolution of Mg–O distances for the oxygen atoms of the bi-carbonate ion. In Simulation **A** the initial coordination of HCO_3^- to the magnesium

was mono-dentate (η^1); in simulation **B** the initial coordination of HCO_3^- to the magnesium was bi-dentate (η^2).

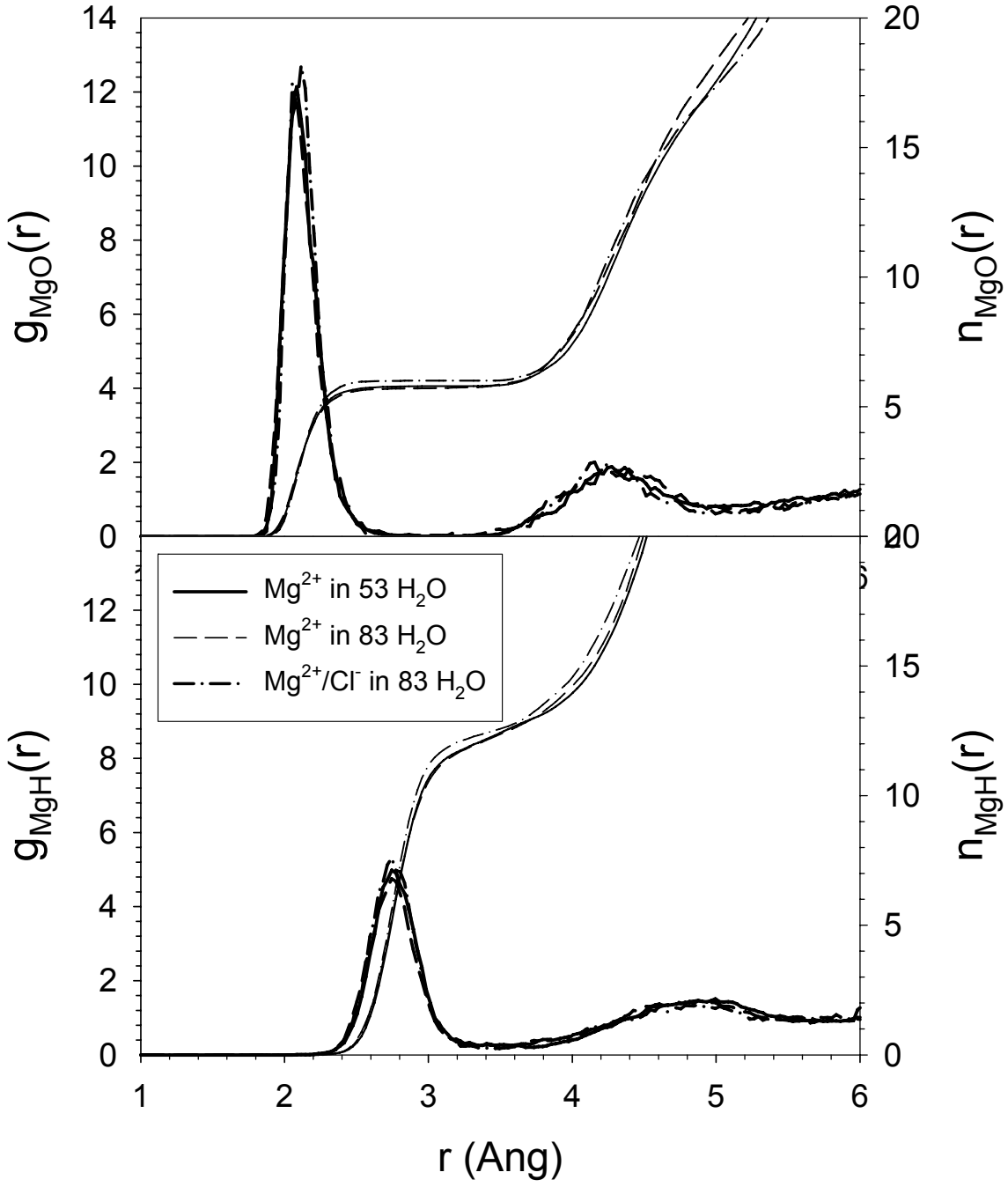

Figure SI.5. Mg−O and Mg−H radial distribution functions, $g(r)$, and running coordination number, $n(r)$, obtained from the CP-MD simulations of Mg^{2+} in 53 H_2O, Mg^{2+} in 83 H_2O and Mg^{2+}/Cl^- in 82 H_2O.

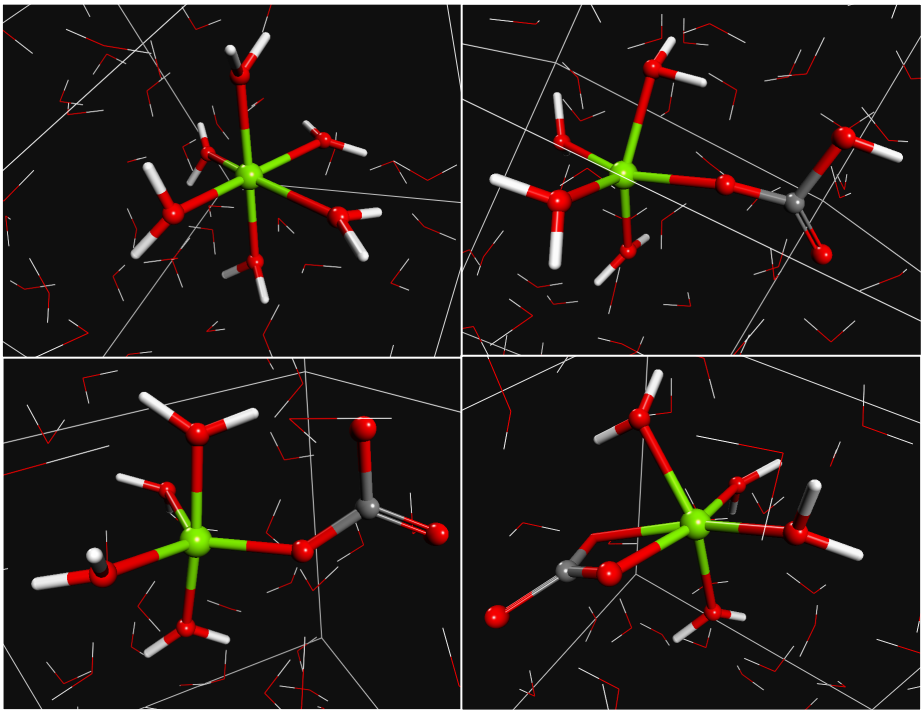

Figure SI.6. Representative snapshot taken from the CP-MD simulations showing the most stable species of the hydrated magnesium ion, and of the solvated magnesium bicarbonate and magnesium carbonate complexes.