Rydberg-type electronic excited states in sodium-doped water clusters

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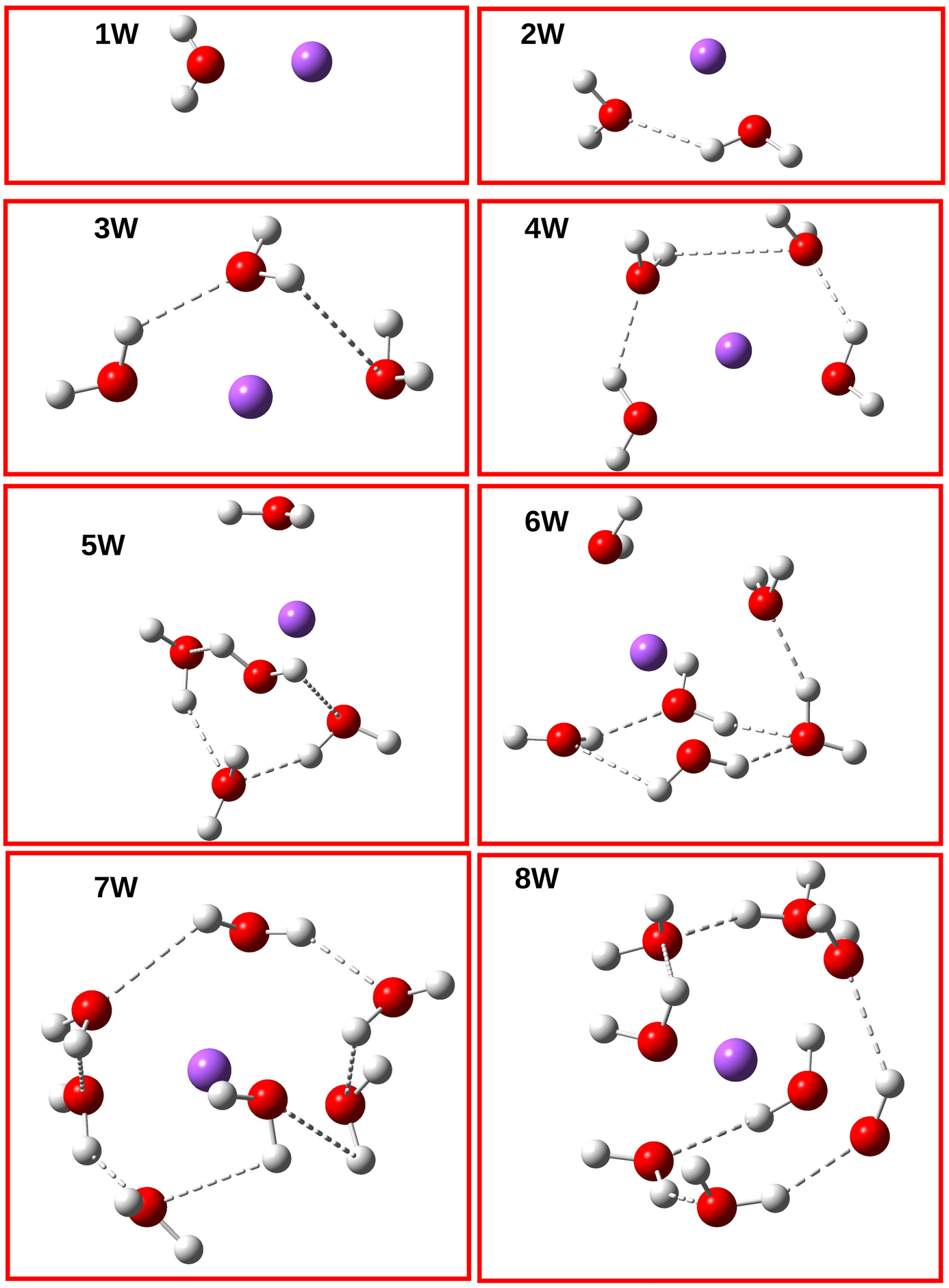
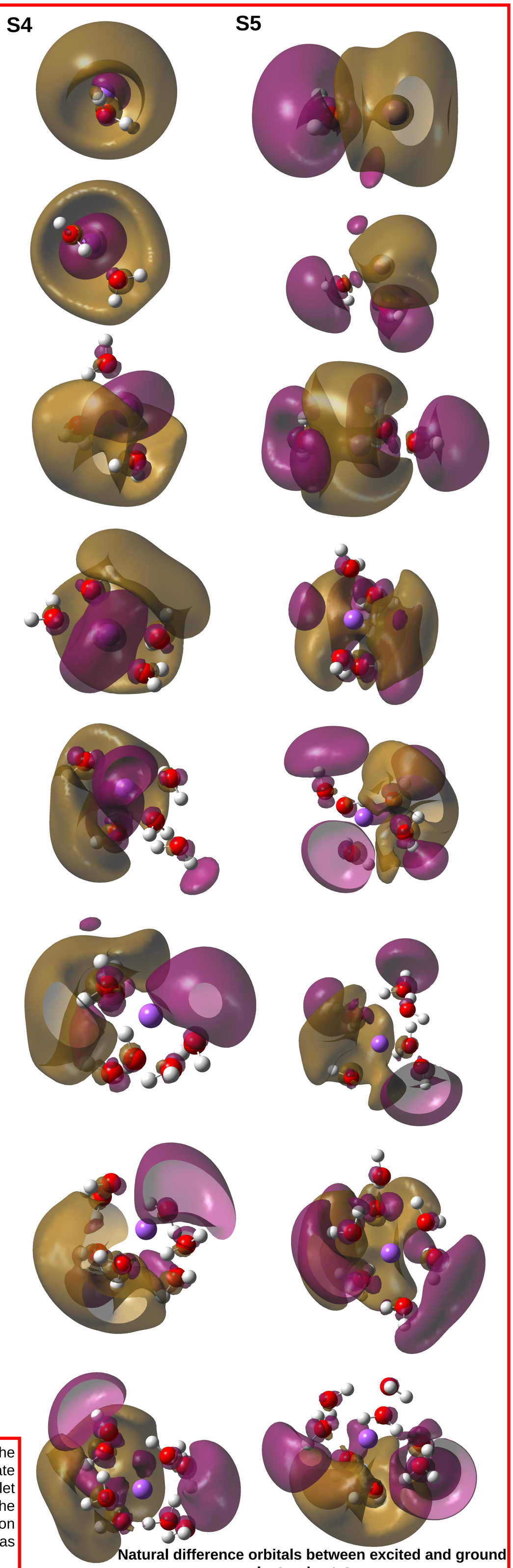
Abstract: Electronic transitions in sodium-doped water clusters were investigated considering the CCSD-type coupled-cluster level of theory. The equation-of-motion coupled cluster method combined with the second similarity transformation expanded on the domain based local pair natural orbitals (DLPNO-STEOM-CCSD) provides an efficient way to calculate excitation energies of the Rydberg-type electronic transitions with high accuracy. The results for different electronic transitions show Rydberg-type orbitals with different special configuration, indicating large delocalization over the water molecules for the 3s1 electron of the sodium atom.

Methods: Back transformed equation-of-motion coupled cluster (**bt-PNO-EOM-CCSD**);
DFT: double-hybrid **wB2PLYP** exchange-correlation functional; Software: Orca 4.2.1; Orca 5.0.1

	S1	S2	S3	S4	S5	S6	IP(vert)	IP(adiab)
1W	1.683	1.697	1.908	3.257	4.464	4.880	4.30	4.23
	1.656	1.670	1.886	3.206	4.514	4.937		
2W	1.472	1.590	1.832	3.156	3.993	4.541	3.96	3.69
	1.413	1.569	1.820	3.145	4.029	4.563		
3W	1.383	1.491	1.844	3.217	3.653	3.716	3.87	3.38
	1.336	1.400	1.771	3.221	3.617	3.705		
4W	1.537	1.835	1.845	3.430	3.545	3.595	3.80	3.27
	1.490	1.710	1.755	3.451	3.506	3.560		
5W	1.504	1.912	2.092	3.281	3.520	3.686	3.83	3.24
6W	1.623	1.995	2.138	3.191	3.553	3.787	3.86	3.21
7W	1.672	1.951	2.376	3.524	3.540	3.749	3.86	3.22
8W	1.578	1.961	2.351	3.610	3.677	3.789	-	-



The geometry structures of Na-(H2O)n clusters



Natural difference orbitals between excited and ground electronic states

Conclusions: Electronic excited state energies obtained at DFT level of theory, considering the wB2PLYP exchange-correlation functional match very well with results computed with accurate wavefunction method considering the back-transformation equation-of-motion coupled cluster with singlet and doublet excitation (bt-PNO-EOM-CCSD) expanded on the localized pair natural orbitals. All of the electronic transitions found for different Na-(H2O)n cluster structures show Rydberg-type excitation character, where due to the excitation the 3s1 electron of the sodium moves on the water cluster. It was also found that the first ionization energy lies mainly between the fourth and fifth excited states.