Ab initio molecular dynamics of Rydberg-type electronic excited state dynamics in small sodium-water clusters

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Ab initio molecular dynamics calculations on a time scale of 20 picoseconds were performed for Rydberg-type excited states of Na (H2O)n (n = 1, .., 5) mixed clusters considering the TDDFT method, including the ωB2PLYP double-hybrid exchange-correlation functional and def2-TZVPD basis set. Fluctuations of the charge and the sodium-oxygen atomic distances predict that, the 3s1 electron of the sodium atom are transferred from the delocalised Rydberg orbitals to the Rydberg orbitals around the water molecules and the sodium atom becomes positively charged with around 0.6e after the first 10 ps. On the other hand, some of the water molecules can move away up to 5 Å from the sodium with a significant negative charge on them. It has been shown that non-radiative relaxation cannot be excluded, they can mostly occur for cases n >= 4. The results confirm that the adiabatic photo-ionisation can occur on the basis of cluster disintegration.