First-Principles Density Functional Theory Investigation of Oxygen and Water Adsorption on the (010), (100), and (111) Surfaces of $BaZrS_3$

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In the last decade, perovskites have attracted remarkable attention as promising alternatives to silicon in the solar industry to achieve more efficient and cost-effective solar cells owing to their outstanding optical and electronic properties and low synthesis costs. However, the conventional hybrid organic–inorganic halide perovskites are highly unstable and toxic, which has hindered their commercialization. Recently, chalcogenide perovskites (CPs) have emerged as promising candidates to overcome these challenges. Among CPs, $BaZrS_3$ has attracted more attention owing to its excellent optoelectronic properties and high stability. However, to guarantee long-term performance under atmospheric conditions, it is important to gain a fundamental understanding of the interactions between $BaZrS_3$ surfaces and atmospheric agents, such as O_2 and H_2O. Herein, we employed density functional theory to study the adsorption of H_2O and O_2 molecules on the (010), (100), and (111) surfaces of $BaZrS_3$. On all three surfaces, the Zr sites were more reactive than the Ba sites towards H_2O and O_2. Generally, O_2 molecules adsorbed more strongly at the Zr sites than H_2O molecules, with significant charge transfer from the interacting surface species. Consistent with their stronger adsorption, O_2 molecules drew more charges from the interacting species than H_2O, oxidizing them to a greater extent. With the surface structures preserved upon H_2O and O_2 adsorption, we observed only small adsorption-induced changes in electronic properties, with the covered surface exhibiting slightly smaller band gaps than the bare surfaces. These results demonstrate a high degree of thermodynamic and atmospheric stability of $BaZrS_3$ surfaces and show that, unlike halide perovskites, the exposure of $BaZrS_3$ thin-film surfaces to H_2O and O_2 molecules may not have significant detrimental effects on their PV performance.