

Sodium Electron Solvation and Reactivity at Water Surface

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Abstract

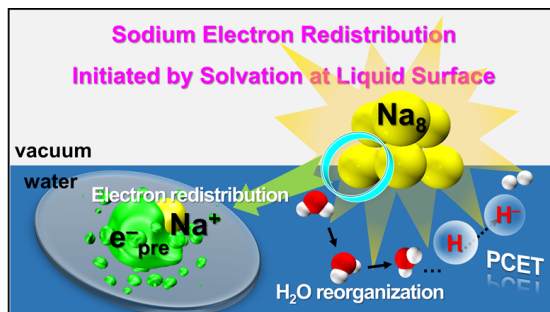
Interfacial solvated electrons (e_{sol}^-) possess profound application values in physics, chemistry, and materials, thus attracting ever-growing attention. Although previous studies have unequivocally corroborated the involvement of e_{sol}^- in the reaction of alkali metals with water, the mechanism has not been thoroughly revealed. Here, we simulate the solvation and ionization process of a single Na or a metallic Na_8 cluster at the vacuum-liquid interface by the hybrid functional-based *ab initio* molecular dynamics (AIMD) method, especially to elucidate the interfacial electron dynamics behavior. Results show that the electron donated by Na or Na_8 is partially solvated at the interface, a process driven by both the Na^+ interaction with the electron and its stabilization in water, which promotes electron redistribution, delocalization, and activation. Additionally, solvation increases the H_2O population near HOMO and on unoccupied orbitals, promoting H_2O reorganization and electron transfer. In aqueous solutions, Na is highly ionized and generates a unique pre-solvated electron (e_{pre}^-). Na_8 cluster, on the other hand, is partially solvated through bottom active O-coordinating sites at the interface, polarizes internally, and produces a pre-solvated dielectron ($e_{2\text{pre}}^{2-}$), which is followed by H_2O reorganization near the surface and the subsequent hydrogen evolution reaction by proton-coupled electron transfer. Surrounding H_2O molecules form multiple Na-O bonds with the remaining Na_8^{2+} to compensate for $e_{2\text{pre}}^{2-}$ loss. Our work displays the microscopic dynamics mechanism of Na and H_2O reaction by AIMD simulation and provides evidence for the participation of e_{pre}^- in the hydrogen evolution reaction, which deepens our attention and understanding of redox reactions involving e_{sol}^- .

Key words: Interface electron solvation, solvated electron, reactivity, proton-coupled electron transfer, *ab initio* molecular dynamics simulation.

1. Introduction

In addition to various inorganic catalytic materials [1-6], solvated electrons (e_{sol}^-), the most reducible particles in nature, play an extremely important role in many fields such as biochemistry, energy and advanced organic chemistry [7-13]. e_{sol}^- are excess

electrons with an s-like ground state formed by solvation and relaxation [14-17]. Generally, e_{sol}^- can disintegrate the solvent structures on their first hydration layer, break chemical bonds and generate other reduction products [10, 18, 19]. At present, it has been disclosed clearly that hydrated dielectrons ($e_{2\text{aq}}^{2-}$) can realize the hydrogen evolution reactions (HER) successfully



in aqueous solutions. This finding provides an intuitive dynamics process for the spontaneous HER induced by ionizing radiation and participated by e_{sol}^- [10]. e_{sol}^- can be generated through water decomposition by laser radiation, two-photon excitation, as well as donation by photoelectron donors represented by I^- and CN^- and other pathways [7, 20-25]. However, the ionization of alkali metals represented by sodium is one of the main means to produce e_{sol}^- in both homogeneous and heterogeneous systems [26-28]. Besides, the gas-phase deposition with Na atoms as neutral precursors can ionize them at the liquid surface, and then release e_{sol}^- into solutions [29]. With the help of gas-phase deposition and molecular beam methods, Gilbert M. Nathanson's group has carried out extensive researches on reduction reactions induced by e_{sol}^- at the gas-liquid interface, such as Benzyltrimethylammonium and glycerol [26, 30-32]. Their studies establish a strategy to explore near-interfacial analogs of radical chemistry in aqueous solutions by evaporating intermediates into gas phase, and also provide information support and method guidance for the mechanism speculation and exploration of the chemical reactions involved e_{sol}^- at the gas-liquid interface and near surface.

Electron transfer (ET) at the solid-liquid interface is of great research value in physics and chemistry, especially in electrochemistry [33-39]. Although the accurate detection of ET information has been allowed by the current development of experimental techniques, it is still necessary to describe ultrafast electron behaviors on picosecond or even femtosecond timescales [38, 40-43]. Studies on ET at the solid-liquid interface focus on photocatalysts/ H_2O , oxides/ H_2O , semiconductor materials/ H_2O in photochemical reactions or $\text{Cu}/\text{H}_2\text{O}$, $\text{Fe}/\text{H}_2\text{O}$, $\text{Au}/\text{H}_2\text{O}$ interface and others [33, 35, 43-49]. Generally, the wide band gap oxides such as TiO_2 , SiO_2 , MgO can be illuminated to excite electrons that are located at the valence band to relax into the water conduction band, then, ET is realized between two phases. Simultaneously, OH^- , H_2 and e_{sol}^- form at the interface [33, 50, 51]. As the typical electron donor, the research on Na atoms is limited to the static calculation or dynamics simulation of a single Na atom in small and medium-sized water clusters or at the liquid surface to characterize its electronic structure [26, 30, 52-58]. With the rapid development of technology means, recent experimental studies have been able to capture the formation process of e_{sol}^- in the reaction of metallic Na with H_2O accurately [59]. The relationship between e_{sol}^- and Na^+ in aqueous solutions and the reactive intermediates in Na and H_2O reactions have also been elucidated and speculated by Car-Parrinello molecular dynamics (CPMD) simulation [60-63]. Unfortunately, although e_{sol}^- have been verified in the reaction of Na and H_2O [59], the Na electronic structure and electron rearrangement before ET between two phases remains an unknown "black box", which has seriously retarded the explanation of classical Na- H_2O reaction mechanism. Therefore, the study of ET behavior at Na/ H_2O interface is necessary.

Moreover, according to Marcus theory, solvent reorganization in solution including molecular structure and orientation changes will significantly influence the ET rate [34, 64]. In the process of ET at the solid-liquid interface, H_2O s solvation is the critical factor. And the successful ET will act on interfacial structures in turn [34, 48, 65, 66]. So the study on synchronous changes of the interfacial structure and electron behavior during the ET process at the solid-liquid interface is important to understand electron transfer mechanism and solvation effect.

In this work, referring to existing experimental and theoretical studies [30, 59, 62, 63], we explore the solvation process of the monomeric Na and Na_8 metallic cluster at the vacuum-liquid interface and in aqueous solutions, and also describe the specific interfacial electron dynamics behavior by ab initio molecular dynamics (AIMD) simulation. Our study uncovers that both Na and Na_8 HOMO electrons can be partially solvated, redistributed, delocalized and destabilized because of the Pauli repulsion between Na valence electron and O lone pair electron, and also be turned into e_{pre}^- and $e_{2\text{pre}}^-$, respectively. More importantly, solvation increases the H_2O population near HOMO and on the orbitals to be occupied, boosting H_2O reorganization and ET. Consequently, HER initiated by Na_8 $e_{2\text{pre}}^-$ occurs with H and H^- anion as intermediates through proton-coupled ET (PCET). Due to multiple Na atoms existence and Na solvation, we conclude that the Na clusters represented by Na_8 are all capable of being pre-solvated and inducing H_2O recombination near the water surface. This study clarifies the electron behavior and reaction mechanism for Na and H_2O reactions and also provides a theoretical basis for the HER involving e_{pre}^- .

2. Simulation details

In this study, the reason why we choose Na atom and a Na_8 cluster as the research objects is shown in the Supporting Information (SI). Since Na_8 has eight Na atoms with a T_d symmetric structure and a low-energy nondegenerate a1 and higher triply degenerate t1 molecular orbitals, it is necessary to reveal the solvation process, phenomenon and results of a single Na atom at the vacuum-liquid interface first. We hope that single Na solvation could provide preliminary information for subsequent studies on Na_8 solvation with more complex geometry variation and molecular orbital evolution information.

We first constructed a periodic box containing 64 H_2O s with a vacuum length of 15 Å. After a long enough time of pre-equilibrium, a periodic representative system with a volume of $12.53 \times 27.53 \times 12.53 \text{ Å}^3$ was extracted. Then, one Na atom or a Na_8 (T_d) metallic cluster was added at 3.4 Å above the water surface, and initial velocities were set as -0.05 Å/fs, that is, make them move towards the water surface (Figure 1) [26, 52].

AIMD simulations under the unrestricted open-shell were carried out by using the CP2K/Quickstep software package [67, 68]. At present, the PBEh40 functional has been widely applied in the research field of e_{sol}^- (Details on the reasons for choosing the PBEh40 functional are provided in the section of **Computational details** in the SI) [10, 33, 54, 69-72]. Therefore, all simulations were done by employing the PBE functional with 40% Fock exchange components [73, 74] and introducing a non-local rVV10 scheme ($b=5.3, C=0.0093$) to describe van der Waals (vdW) interaction [73, 75, 76]. The core electrons of each element are described by the Goedecker-Teter-Hutter (GTH) mode-conserving pseudopotentials [77] and the valence electrons are described by the Gaussian mixed plane wave basis set (GPW) [77]. The Kohn-Sham (KS) orbital is expanded into a TZVP-type Gaussian basis set, and the electron density is truncated to a plane wave basis set of 300 Ry [78]. At the same time, the auxiliary density matrix method (ADMM) based on the cFIT3 auxiliary basis set [79] is used to effectively reduce the computational resource consumption. The dynamics simulations were performed with a time step of 0.5 fs, and the temperature was controlled at 350 K utilizing a canonical (NVT) ensemble and a CSV thermostat [80].