

Charge transfer between molecules and metal surfaces covered with ultrathin insulating films

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The main feature behind photovoltaic devices, in the framework of organic electronics, is the presence of a stable molecular system in which solar radiation can easily induce electronic transfer. These systems can be constructed by deposition of organic molecules on metal surfaces as well as on metal surfaces covered by insulating layers, thus providing a donor-acceptor set with the possibility of charge transfer between them induced by light [1]. Charge transfer processes lead to level alignment of the frontier orbitals but they may also induce structural transformations. Therefore, a first step towards the design of photovoltaic devices implies an accurate description of the structure and the charge transfer on the ground state.

In this communication we present the results obtained in a theoretical study on the interaction between different organic molecules, with potential photovoltaic activity, and clean metal surfaces or metal surfaces covered by ultrathin ionic layers. We have studied several organic molecules deposited on two metal surfaces - Cu(100) and Ag(111). These systems cover a large range of typical metal-surface interactions: from weak van der Waals interactions to strong covalent binding. Furthermore, we have included NaCl monolayers(ML) as an insulating thin film.

In particular, we have studied C₆H₆/Cu(100), which is a prime example of the interaction between organic molecules, with π -delocalized electrons, and a metal surface. In order to check the effect of insulating films, we have also studied C₆H₆/*n*MLNaCl/Cu(100); (*n* = 1, 2 and 3). Our study also includes C₆₀/Cu(100) and C₆₀/*n*MLNaCl/Cu(100), where not only the study is interesting itself, but also the computational challenge that it supposes. Finally, we have computed the interaction of self-assembled organic monolayers of tetracyanoquinodimethane (TCNQ), tetrathiafulvalene (TTF), and TCNQ + TTF on Ag(111). In all these systems we evaluated the structural rearrangement after adsorption, charge transfer and decoupling of the organic molecule from the surface. We will compare our results with recent experimental measurements [2] and previous works [3-6]. Density Functional Theory (DFT) calculations were performed with a plane-wave, ultrasoft pseudopotential method as implemented in the VASP code [7]. The projector augmented wave (PAW) method has been used together with the Perdew-Wang91 functional [8]. Van der Waals dispersion forces have been taken into account with the DFT-D2 method of Grimme [9].

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