Model studies of the structure and optical properties of the TiO$_2$(110) surface with an adsorbed Ag atom

Tijo Vazhappilly [a] , Maria Pilar de Lara Castells [b], and David A. Micha [c]

[a] Theoretical Chemistry Section, Bhabha Atomic Research Centre, Mumbai 400085, India
[b] Instituto de Fisica Fundamental (C.S.I.C.), Serrano 123, E-28006 Madrid, Spain
[c] Departments of Chemistry and of Physics, Quantum Theory Project, University of Florida
Gainesville, Florida 32611, USA

Light absorption by materials based on TiO$_2$ without and with adsorbates is a fundamental process leading to electronic rearrangement, including electron transfer at the surface and photoinduced conductivity. Understanding these phenomena is important in connection with photoelectrochemical cells. The present preliminary studies deal with the structure of the atomic Ag adsorbate on the substrate TiO$_2$(110) , and with the appearance of new band states on the surface of the adsorbate system. Recent results show that the binding position and energy of a heavy noble gas atom on this substrate must be done including dispersion (van der Waals) corrections [1] and, consequently, the present studies explore the importance of dispersion energies for the structure of adsorbed Ag atom, using density functional theory supplemented by the dispersion term, within the PBE-D3 treatment [2]. Also, recent work on photoexcitation of Ag adsorbed on Si surfaces [3] indicates that light absorption excites valence electrons in the solid into atomic Ag orbitals, where they are localized. This leads to the appearance of holes in the valence band and an increase in photomobilities, as obtained from a time-dependent reduced density matrix (RDM) method [3]. It is of interest to explore whether a similar photo-effect is present in the present system. With this aim, we obtain the electronic density of states (EDOS) without and with Ag adsorbed on the TiO$_2$(110), to ascertain whether a similar change on the density of valence, conduction, and intraband states appears here. This is done first with a calculation using a hybrid DFT, the HSE06 functional, which is known to provide good values for the band gap of the substrate. Compared with PBE results, a correction to band gaps is identified and used in an efficient PBE+BG procedure to generate accurate EDOSs. This procedure and the RDM can be used to generate light absorption intensities versus light wavelength, and also photomobilities of holes and electrons.

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