**Model studies of the structure and optical properties of the TiO₂(110) surface
with an adsorbed Ag atom**

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The present studies of the atomic Ag adsorbate on the substrate TiO₂(110) explore the importance of dispersion (or van der Waals) energies for determining the structure of adsorbed Ag atom, using density functional theory (DFT) supplemented by a dispersion energy treatment, within the PBE-D3 treatment. It is also of interest to explore electronic excitation by light absorption. Electronic density of states (EDOS) are obtained without and with Ag adsorbed on the TiO₂(110), to find the extent of change on the density of valence, conduction, and intraband states. This is done using the hybrid HSE06 functional, which is known to provide good values for the energy band gap of the substrate. A computationally efficient PBE+BG procedure **for these structures, which corrects the PBE band gap**, is implemented to generate accurate EDOSs and light absorption intensities versus photon energies. This is followed by a reduced density matrix treatment of the dissipative dynamics of light absorption, generating state-to-state oscillator strengths and photoabsorbances for the pure and nanostructured TiO₂(110) surfaces. Adsorption of Ag leads to a noticeable increase in light absorption at visible wavelengths, and very large increases in the UV region of the spectrum.

Keywords: titanium dioxide; silver adsorbate; surface structure; optical properties; density functionals; van der Waals dispersion energies; reduced density matrices; light absorbance.

1. Introduction

Light absorption by materials based on TiO₂ 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 photocatalysis, such as for production of hydrogen or water splitting, and in the design of photoelectrochemical cells [1]. Very active related research has been the subject of several recent reviews [2-5]. The present preliminary studies deal with the structure of an atomic Ag adsorbate on a substrate TiO₂(110) rutile surface, and with changes in light absorption due to the appearance of new energy band states on the surface of the adsorbate system. These studies combine ab initio density functional theory (DFT) and reduced density matrices, with an extension of DFT needed to include dispersion energies.

Recent results have shown that the binding position and energy of a heavy noble-gas atom, Xe, adsorbed on this substrate must be done including dispersion (van der Waals)

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corrections [6], and that density functional treatments can provide bonding results in agreement with accurate many-electron treatments provided they are corrected by including long-range van der Waals attraction energies, which give shorter bond distances and stronger binding. It was demonstrated there that a quantitative agreement between theoretical and experimental estimations of binding energies can be achieved by using a so-called DFT-D3 dispersion correction [7]. Previous studies of He adsorbed onto $\text{TiO}_2(110)$, using cluster and periodic slab models and many-electron post-Hartree-Fock treatments as well as DFT, have shown the importance of including the dispersion energy contribution to adsorbate-surface interaction energies [8]. Also, more recent work on the $\text{Ag}_2/\text{graphene}$ interaction showed that the PBE-D3 treatment provides potential energy surfaces following closely those estimated at higher ab-initio level [9].

The dispersion corrected results allow comparison of adsorbate binding energies at different surface sites and show that noble gas atoms prefer to adsorb on top of the Ti atom, in agreement with experimental observations. Theory shows that this can be understood as resulting from the balance of short-range repulsive forces and long-range attractive ones, which favors the on-top location where repulsive forces are smaller.

The present studies explore the importance of dispersion energies for the structure of sites with an adsorbed Ag atom, an open-shell species, using density functional theory supplemented by the dispersion term, within the PBE-D3 treatment. Two versions of D3 are available with different functions used to damp long-range van der Waals interactions at short distances [7], called D3(0) for a damping function going to zero at the origin of intermolecular distances and D3(BJ) for a function going instead to a constant value. The results presented here for on-top, bridge, and hollow sites on the surface were obtained with the D3(0) version. They allow us to identify the site of largest binding for this adsorbate with open electronic shells, unlike noble gases, and to understand the roles of intermolecular forces in the outcome.

Also, recent work on photoexcitation of Ag adsorbed on Si surfaces using a combination of ab initio DFT and reduced density matrix methods (RDM) [10-12] 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 photoabsorbance, photovoltage, and photomobilities, as obtained from the equations of motion in the RDM method. It is of interest to explore whether a similar photoabsorbance effect is present in the present adsorbate system, with Ag as the adsorbate and $\text{TiO}_2(110)$ as the substrate.

With this aim, we generate DFT orbitals and oscillator strengths to obtain electronic density of states (EDOS) without and with Ag adsorbed on the $\text{TiO}_2(110)$, to ascertain whether a similar change on the density of valence, conduction, and intraband states appears here, and to calculate light absorbances versus photon energies in the visible and UV regions of the electromagnetic spectrum. This is done first with a calculation using a hybrid DFT, the HSE06 functional [13], which is known to provide good values for the band gap of the substrate. Compared with PBE results, a correction to the band gap is identified and used in a PBE+BG procedure [10] [we have found to be computationally efficient for the optical properties of](#)

semiconductor surfaces, and necessary to generate accurate EDOSs and light absorption intensities versus photon energies. This procedure and the RDM can also be used to generate photomobilities of holes and electrons, a subject which is not included here.

The present model calculations have all been done for the rutile structure of TiO_2 . A previous computational study was done for a Ag_2 adsorbed on the surface of TiO_2 with the anatase structure, generating a slab by periodic translation of a $\text{Ag}_2\text{Ti}_{30}\text{O}_{72}\text{H}_{16}$ supercell [14]. This employed a theoretical treatment similar to ours using however the PBE functional, and the reduced density matrix treatment for detailed calculations of intensities of photoabsorption and relaxation, but did not address the importance of dispersion energies for the adsorbate structure.

The optical properties of the rutile and anatase structures with a variety of dopants, obtained from experimental and computational works, have been reviewed in recent reports [15,16]. However they do not address the question of the importance of dispersion energies for surface structures or the role of intraband adsorbate states which are the subjects of the present work. This study for a well defined structure with a single adsorbed Ag atom allows detailed exploration of surface structure and optical properties, and clarifies some issues generally relevant to the field.

2. Structures of Ag on $\text{TiO}_2(110)$

The crystal supercell of pure rutile TiO_2 chosen for our model is orthorhombic with 64 Ti and 128 O atoms, with a planar 4 X 2 supercell face of rutile TiO_2 perpendicular to a z-axis and four layers. A lattice slab is generated by periodic translation of the supercell along (x,y) axes. Atomic Ag adsorbs on the rutile $\text{TiO}_2(110)$ surface at on-top, bridge, and hollow positions, with structures of different bond distances and binding energies, and it is of interest to find which structure has the largest binding energy.

In some detail, calculations are done with a periodicity along z of 29 Å, including a vacuum space of 16 Å added along the z-axis to avoid interaction between repeating slab structures in the z direction. The lattice parameters along x and y are 11.940 Å and 12.991 Å, respectively. The adsorption geometries and other properties are calculated using periodic density functional theory employing plane wave basis sets. All the calculations have been performed with the Vienna Ab initio Simulation package (VASP) [17]. The standard projector-augmented-wave (PAW) potentials have been used for O and Ag in our calculations [18] while for the Ti atom a PAW potential is used where 3p and 3s electrons are also treated as valence electrons in addition to 3d and 4s electrons. Grids of points in reciprocal space have been generated with kinetic energy cut-off for the plane wave basis sets chosen as 700 eV. The Brillouin zone has been sampled at the Gamma point only.

In one set of calculations, the exchange-correlation electronic interactions have been modeled by the Perdew-Burke-Ernzerhof (PBE) functional [19]. For the adsorption of a Ag atom

on the TiO_2 surface, we optimized the Ag position on top of Ti, at a bridged O atom and at a hollow of the TiO_2 slab. In all our simulations, the TiO_2 slab structure has been kept fixed. The PBE functional tend to underestimate the band gap and optical properties of materials due to self-interaction errors. To overcome this issue, a second set of calculations have been performed using the hybrid HSE06 functional [13] on the same adsorption geometries obtained from PBE calculations.

A single Ag atom on top of Ti gives a structure with a Ag-Ti bond length = 2.92 Å (no D3), and Ag-Ti bond length = 2.78 Å (with D3), and supercell views along the z-axis perpendicular to the surface and along the x-axis are shown below in Figure 1 (a) and (b) respectively.

Figure 1(a)

Figure 1(b)

Figure 1. A Ag atom (grey) on top of Ti (blue), for the supercell of the rutile $\text{TiO}_2(110)$ with 64 Ti and 128 O atoms, with O in red, viewed along the z-axis in top view 1(a) and along the x-axis in side view 1(b). The supercell is periodically translated along x- and y-axes to generate a slab.

A single Ag atom on a bridge oxygen for the same supercell is shown in the following Figure 2 (a) and (b). Calculated values with the PBE functional are Ag-O bond length = 2.17 Å (with no D3), and Ag-O bond length = 2.14 Å (with D3).

Figure 2(a)

Figure 2 (b)

Figure 2. A single Ag atom is shown in top and side views adsorbed on a bridge oxygen of the rutile $\text{TiO}_2(110)$, at the supercell with 64 Ti and 128 O atoms.

The third investigated structure has Ag adsorbed on a hollow site as shown in Figures 3(a) and (b), obtained with the PBE functional and giving Ag-Ti bond lengths = 3.45 , 3.45, 3.36 Å , and a Ag-O bond length= 2.25 Å, with PBE-D3(0).

Figure 3 (a)

Figure 3 (b)

Figure 3. An adsorbed Ag at a hollow site, in top and side views, for the same supercell of the rutile $\text{TiO}_2(110)$.

In all cases, results show that including dispersion energies lead to significantly shorter bond lengths and larger binding, for all three binding sites.

3. Adsorbate binding including dispersion energy, and excited electronic levels

Energy levels of HOMO and LUMO orbitals, total binding energies, and adsorption energies from DFT calculations with PBE, PBE-D3, and HSE06 functionals, for TiO_2 and for Ag on TiO_2 are summarized in Table 1 as follows. Results here have been obtained with the D3(0) functional form for the dispersion energy, which is zero at the origin of the interatomic distance as defined in [7]. The Table allows comparisons for two different aspects of the calculations; one is the order of binding energies for the three mentioned structures (on-top, bridge, and at hollow) and the other is the magnitude of energy band gaps for the structures.

Comparing PBE and PBE-D3 results it is possible to ascertain the importance of dispersion energies, and indeed these are critical to determination of the site of largest binding. Results from PBE give the largest binding for Ag on the bridge but not by much over the hollow location. However when dispersion energies are added we find that the hollow location is the one with the largest binding. This is consistent with the expectation that for an open shell atom like Ag, binding is larger when it is located near more neighbors and there are more dispersion attraction contributions. This appears to also be the conclusion from calculations of Ag on the anatase phase $\text{TiO}_2(101)$ surface [20]. Here the adsorption energies come from $E_{\text{AgTiO}_2} - E_{\text{TiO}_2} - E_{\text{Ag}}$, all

obtained with the same DFT functional, and with the same grid of points in reciprocal space for the plane wave expansions.

The Table gives occupations of highest occupied and lowest unoccupied energy levels and distinguishes the HOMO with occupation 2, named HOMO(2) or HO2, from the HOMO(1) or HO1, with occupation one. The band gap is defined for all the structures as the difference $E(\text{LU}) - E(\text{HO2})$ to compare cases without and with adsorbed Ag, and the $E(\text{HO1})$ is found to be just below the bottom of the conduction band (CB) given by $E(\text{LU})$, and the difference $E(\text{LU}) - E(\text{HO1})$ can be described as an adsorbate intraband energy. This $E(\text{HO1})$ level location is similar to the level location of dopant states in a doped semiconductor, such as one finds for the donor impurity as in Si, an n-type Si structure [23]. Given that the best estimates from calculated and measured values of the band gap energy for bulk TiO_2 are 3.0 eV for rutile and 3.2 eV for anatase, with larger values for confined electron structures [16], it is clear from our Table 1 that this value is correctly found with HSE06 but is greatly underestimated by PBE.

The HSE calculations can also be done if needed adding the D3 dispersion corrections, and give a reversal of the values in the table for bridge and hollow positions, with the hollow site again the one with the largest binding. However, for the purpose of finding energy levels and generating electronic orbitals the HSE06 results are reliable and energy differences are similar even after addition of dispersion energies. Therefore, the related electronic density of states (EDOS) and light absorbances calculated in what follows from orbitals generated by HSE do not include dispersion since the density of levels it is not likely to change due to such correction. Here we present results based on Gamma point values.

Table 1. Highest occupied level energy with double and single occupancy, lowest unoccupied level, band gap (as defined in the text) from those levels, and adsorption energy, for pure TiO_2 and adsorbate Ag/ TiO_2

System	HOMO(2) energy (eV)	HOMO(1) energy (eV)	LUMO energy (eV)	Band gap (eV)	Total energy (eV)	Adsorption energy (meV) $E_{\text{AgTiO}_2} - E_{\text{TiO}_2} - E_{\text{Ag}}$
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1. TiO₂ fixed and Ag moved						
PBE						
Gamma point only						
Pure TiO ₂	-1.9796		- 0.0236	1.956	-1705.8466	
Ag on top of Ti	-1.8118	-0.0365	0.1335	1.9453	-1706.2809	-396
Ag on bridge O	-1.6564	0.3120	0.3468	2.0032	-1706.5441	-659
Ag at hollow site of TiO ₂	-1.7331	0.2065	0.2628	1.9959	-1706.5317	-646
2. TiO₂ fixed and Ag moved						
PBE-D3 (Dispersion included)						
Gamma point only						
Pure TiO ₂	-1.9796		- 0.0236	1.956	-1732.9236	
Ag on top of Ti	-1.8119	- 0.0482	0.1345	1.9464	-1733.8707	-908
Ag on bridge O	-1.6535	0.3160	0.3507	2.0042	-1733.9944	-1032
Ag at hollow site of TiO ₂	-1.7340	0.2055	0.2616	1.9956	-1734.1251	-1163

3. TiO₂ fixed and Ag moved						
HSE06 (No dispersion corrections)						
Gamma point only						
Pure TiO ₂	- 3.0391		0.4269	3.466	-2109.8352	
Ag on top of Ti	-2.8612	0.2196	0.5967	3.4579	-2110.3076	-382
Ag on bridge O	-2.6852	0.7266	0.7901	3.4753	-2110.5756	-650
Ag at hollow site of TiO ₂	-2.7855	0.5950	0.6741	3.4596	-2110.5582	-632

The addition of Ag to the crystal to form a periodic, nanostructured slab surface, leads to the appearance of new adsorbate band energies. Here the result of calculations are shown only for the Gamma point, the center of the Brillouin cell in reciprocal space. The energy bands are generally flat and values shown for the Gamma point are typical. This was tested doing calculations with a Gamma-centered 5x5x1 k-point mesh, giving adsorption energies that differed by only ca. 0.005 eV from the single Gamma point values at the potential minimum for the Ag to surface equilibrium distance.

Several computational studies have been done to obtain results for comparisons, in addition to the results listed in the Table. They relate to the relaxation of substrate atomic positions near the adsorbate, electronic spin polarization, and extent of electronic density transfer between adsorbate and substrate. Relaxation of Ag-Ti, and Ag-O bond distances with PBE+D3(0) show small changes in bond distance, of the order of a few hundredths of an Angstrom, but sizable changes in total binding energies of the order of 0.1 eV. Differences of total binding energies however give adsorbate values comparable to the ones without relaxation and are expected to keep the same order in relative magnitude of adsorbate energies.

Calculations were done for selected structures without and with electronic spin polarization for comparisons. These have shown that spin polarized states give larger total binding energies for both pure TiO₂ and adsorbate Ag/TiO₂ but that their differences are of the same magnitude as for non-polarized results. Electronic densities from PBE+D3(0) calculations have provided net charge densities for Ag at the three locations of interest, with net positive charges of 0.449, 0.488, and 0.239 for the hollow, on the oxygen bridge, and on top of Ti, respectively. These indicate that electronic charge has migrated from the Ag adsorbate to the TiO₂ slab, in the ground electronic state of the three structures.

4. Electronic Density of States (EDOS) from PBE and HSE06 Functionals

Electronic density of states (EDOS) $D(\varepsilon)$ have been generated from the locations of energy levels ε_j obtained from the DFT calculations, with a Lorentzian line shape as

$$D(\varepsilon) = \sum_j \frac{w}{2\pi} \frac{1}{(w/2)^2 + (\varepsilon - \varepsilon_j)^2}$$

where w is the full-width at half-maximum coming from the interaction of electronic transitions at the adsorbates with charge density fluctuations in their medium and the related line broadening due to their relaxation rates. The value $w = 20$ meV has been chosen here as a parameter based on known measured and calculated values for relaxation times [19,20]. Electronic density of states (DOS in eV^{-1}) of a Ag atom adsorbed on top of a Ti atom of TiO_2 , on a bridge oxygen atom, and at a hollow of the (110) surface are shown in Figure 4 obtained from PBE-D3, and HSE06 functionals, with the common origin in the energy scale chosen for convenience in the figure.

Figure 4. Electronic density of states (DOS) for the four considered structures, from orbital energies calculated with the PBE-D3 and HSE06 functionals.

This Figure shows the large differences between the EDOS from the two functionals, with the correct results from HSE06 for the band gaps and with maxima in valence and conduction bands in different locations versus electronic energies. The tails of the Lorentzian distributions give small contributions into the band gaps, and small peaks due to the adsorbate levels just below the conduction band bottom are present but not visible in the present scale.

5. Reduced density matrix treatment of light absorbance

Light absorption in the region of the adsorbate atom involves the electronic dissipative dynamics of the atom in a supercell interaction with its medium, and can be described starting with an statistical density operator treatment followed by a reduction procedure to decrease the number of electronic degrees of freedom. This allows treatment of the one-electron dynamics and feasible calculations using a basis set of Kohn-Sham orbitals from a chosen DFT.

The equation of motion for the reduced density matrix (RDM) with Kohn-Sham orbitals as a basis set in the Schrödinger picture and $\mathbf{F}$ the mean-field Hamiltonian matrix is

$$\frac{d\rho_{jk}}{dt} = -\frac{i}{\hbar} \sum_l (F_{jl}\rho_{lk} - \rho_{jl}F_{lk}) + \left(\frac{d\rho_{jk}}{dt}\right)_{diss}$$

where the last term is the dissipative rate obtained in our case within the Redfield approximation valid for fast relaxation and time evolution of the RDM after relaxation ends [24]. This equation of motion (EOM) can be solved for steady light absorption introducing a rotating-wave reference frame and the rotating wave approximation, which time-averages out rapidly varying terms. We follow here the treatment developed in Ref.[19]. The resulting RDM is $\tilde{\rho}_{jk}$ and its EOM can be solved when $d\tilde{\rho}_{jk}/dt = 0$ to obtain steady state values for the diagonal elements of the reduced density matrix including dissipation due to charge density fluctuations. They are given in the rotation frame by

$$\tilde{\rho}_{jj}^{ss} = 2 - 2\Gamma_j^{-1} \sum_{k=LUMO}^{\infty} g_{jk}, j \leq HOMO$$

$$\tilde{\rho}_{jj}^{ss} = 2\Gamma_j^{-1} \sum_{k=0}^{HOMO} g_{jk}, j \geq LUMO$$

$$g_{jk}(\Omega_L) = \frac{\gamma_{jk} \Omega_{jk}^2}{\gamma_{jk}^2 + \Delta_{jk}(\Omega_L)^2}$$

where generally Γ_j is a depopulation rate (of order 1 ps), γ_{jk} is a decoherence rate (about 27 fs), Ω_{jk} is the Rabi frequency due to coupling of the external light field to the transition dipole D_{jk} , $\Delta_{jk} = \Omega_L - \Omega_{jk}$ is the detuning frequency, and Ω_L is the light frequency for photons of energy $\hbar\Omega_L$, with the above rate values typical for photoinduced electronic transitions coupled to dissipative phonons and excitons in the medium.

Results for the light absorption flux density $F(\hbar\Omega_L)$ as a function of the photon energies $\hbar\Omega_L$ have been obtained here for a distribution $f_{sol}(\Omega_L; T)$ of photons corresponding to the solar flux absorption intensity, from a black body radiation at temperature $T = 5,800$ K, as [10,11]

$$F(\hbar\Omega_L) = \sum_{\substack{j \text{ occ} \\ k \text{ unoc}}} \frac{\overline{f_{jk}}(\tilde{\rho}_{jj}^{ss} - \tilde{\rho}_{kk}^{ss})\hbar\gamma f_{sol}(\Omega_L)\hbar\Omega_L}{2\pi[(\hbar\Omega_L - \hbar\Omega_{jk})^2 + (\hbar\gamma/2)^2]}$$

with $\overline{f_{jk}}$ an oscillator strength per active electron **calculated from a state-to-state transition dipole and normalized as in Ref. [10]**, $\hbar\Omega_{jk} = D_{jk}\mathcal{E}_L$ and $\hbar\gamma = 0.01$ eV. Its units are W/(cm².eV).

Calculations with these equations can be done using either PBE or HSE06 orbitals and matrix elements, with PBE requiring less computational time as compared to the hybrid functional HSE. In our previous work we have verified that the PBE orbitals can be used in a procedure where the band gap difference between PBE and HSE06 has been corrected by shifting the conduction band levels of PBE by the proper amount of band gap energy. This procedure called PBE+BG has been found [10,11] to give results in very good agreement with selected HSE results **for semiconductors**, and is used here. Results for the four systems considered here, of light absorption flux density versus photon energy are shown in Figure 5.

Figures 5. Light absorption flux density in units of $W/(cm^2.eV)$ obtained from transition dipoles generated with orbitals calculated with HSE06 and PBE functionals. The PBE results for the excited states have been corrected by addition of a band gap term and labelled PBE+BG.

A main observation is that adsorbing Ag on the surface of TiO_2 leads to absorption peaks that are typically double the values for pure TiO_2 , and that the integrated light absorption intensity for photon energies up to the calculated 5 eV is much larger. The Figure panels show small amounts of light absorption even below the band gaps listed in Table 1 from contributions on the long tails of the Lorentzian distributions in $F(\hbar\Omega_L)$, and also due to contributions of transitions from the singly occupied HOMOs with energies just below the bottom of the conduction band, into the conduction bands. These are relatively small and do not show in the scale of the Figure but are very significant insofar they show light absorption in the region of the visible and near IR spectra important for sunlight capture.

6. Conclusion and Ongoing Work

We have considered two properties of systems with a Ag atom adsorbed on the rutile $\text{TiO}_2(110)$ surface, namely the structures of the adsorbate and how its presence affects the intensity of light absorption. The different atomic structures of the adsorbate and their optical properties have been modeled using density functional theory with two different functionals and also adding dispersion energy corrections. This has allowed us to identify the location of largest binding and has given related bond lengths. Light absorption intensities have been obtained to compare pure and adsorbate compounds, accounting for electronic dissipative dynamics within a reduced density matrix treatment and looking for steady state solutions of the RDM equation of motion. Some of the conclusions are as follows.

Calculations including dispersion energies are needed to identify the location with largest binding energy. They give shorter bond distances and larger adsorption energies, and alter the order of binding energies among on-top, bridge, and hollow structures. Also, the adsorption energy differences are reduced upon inclusion of the D3 dispersion. The structure of largest binding has Ag at the hollow in the (110) surface. This is in contrast with previously known results for noble gas atoms which adsorb on top of Ti. Physical arguments can be used to understand these results, looking into the balance between short-range repulsion and long-range attraction forces and the number of nearest neighbors. For the present open-shell Ag atom, the hollow location increases the number of nearest neighbors and the total attraction forces. Here in addition attractive dispersion-less energy terms (electrostatic and induction energies) are also relevant for the binding, and lead to polarization of the silver atom electronic charge towards the substrate. For the noble gases on the other hand, being on top of the Ti surface atom decreases the number of neighbors and diminishes the repulsion forces, while their potential minimum is determined by a balance between the exchange-repulsion and the dispersion contributions.

As expected, the hybrid HSE06 functional gives larger band gaps than PBE for pure TiO_2 , in agreement with known measured values. This has a large effect on the electronic density of states which appear in optical properties, and indicates that DFT functionals must be chosen carefully to describe these properties. When Ag is added, new energy bands appear just below the conduction band bottom, similarly to what is found for n-doped semiconductors. The **several computational studies done to obtain results for comparisons, in addition to the results listed in the Table 1, relate to the functional form for the dispersion energy, relaxation of substrate atomic positions near the adsorbate, electronic spin polarization, and extent of electronic density transfer between adsorbate and substrate. They generally give small changes in bond distances and in the relative values of adsorbate energies.**

The new intraband energy levels that appear when Ag is added allows for photoexcitations at photon energies quite smaller than the band gap of pure TiO_2 . **It is in principle possible to analyze what electronic states are involved in the intensities of photoexcitations, by identifying what state-to-state transitions have large oscillator strengths, but these details are yet to be**

obtained. Qualitatively, it is expected that the largest intensities result from transitions from the occupied orbitals of Ag to the unoccupied Ti 3d conduction band states.

The reduced density matrix treatment combined with a proper ab initio density functional treatment provides light absorbance, and shows adsorbances of AgTiO₂ much larger than for pure TiO₂. Using the computational procedure PBE+BG is an efficient and accurate computational alternative for generating the electronic density of states and excited orbitals of semiconductors. Other aspects of optical properties relevant to photoelectrochemistry, such as the values of lifetimes of the holes and excited electrons created by light absorption, can also be obtained from the combined DRM and DFT treatment solving the equations of motion for the RDM with a generalized response theory suitable for non-equilibrium phenomena induced by light [25].

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