A Theoretical Study of the Role of Interfacial Water and Triboelectric Charging in Insulators

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Abstract

In electrophotographic printing, the adsorption of water on critical surfaces has an overwhelming but poorly understood effect on the triboelectric charging. In this work, Molecular Mechanics was used to find the most probable water adsorption sites for isolated PMMA, poly(methyl methacrylate), and isolated silica models, and for intermolecular complexes between PMMA and silica which are responsible for triboelectric charge transfer. Density functional theory (DFT) was used calculate the local energy minima, the adsorption of water molecules on different surface functional groups, and the analysis of the frontier orbitals, to quantitatively compare the energy gap differences for electronic charge transfer, and thus the effect of hydration site on PMMA and silica on electronic charge transfer.

Four surface water adsorption modes that affect electron charge transfer between PMMA and silica were found: water adsorbed on the PMMA carbonyl, water adsorbed at the active site of the LUMO on silica, water as a spacer between PMMA and silica, and water as a charge carrier dissipating charge.

This work provides a detailed mechanistic understanding of the effect of water on the surface electronic structure of amorphous silica and PMMA that are critical to electrophotographic applications, and no doubt to other applications where the surface electronic structure is relevant.

Experimental

A one layer cylinder-like silica model ($Si_{12}O_{32}H_{16}$) with all silicon atoms in tetrahedral geometry was used to represent an untreated silica surface, which will be a simple model for a toner silica surface additive. The cylinder is edge terminated by two hydroxyls to represent the geminal silanols [$Si(OH)_2$], which are typical of the β–cristobalite (100) surface that has been identified experimentally on the amorphous silica surface [1,2,3]. A trimer was used to represent the PMMA polymer, which represents the surface polymer coating on a simple model carrier. To distinguish the effect of functional group orientation (alkyl vs. carbonyl), all three carbonyl groups were designed to coordinate to the same side, allowing two orientations of the carbonyl groups with respect to the contact interface. Calculations were performed with the DMol3 module from the Accelrys Materials Studio 4.2 [4] using DFT with Perdew's 91 generalized gradient approximation (PW91PW91) [5], and a double numerical basis set with d-polarization functions (DND) [6].

Results and Discussion

Previous work [7,8] has shown the promise of QM methods, including DFT, to understand charge transfer in insulators, and the relationship of surface materials properties with the donor and acceptor sites [8,9,10]. In our previous study [8], illustrated in Fig. 1, it was demonstrated that electron transfer can be predicted by a model where there is a charge precursor complex of two materials in contact, and where in both materials the HOMO (or in some cases its excited states, HOMO-n) is the electron donor for charge exchange, and the LUMO (or in some cases its excited states, LUMO+m) is the electron acceptor for the electronic charge exchange. Thus electronic charge exchange will occur in both directions: from the HOMO(-n) on surface A to the LUMO(+m) on surface B, and from the HOMO(-n) on surface B to the LUMO(+m) on surface A. The net charge transfer is contribution of both processes, the lower energy gap will be denoted the forward charge transfer gap, the higher the reverse energy gap. The net charge exchanged depends on the difference in energy gap of these two processes, smaller gaps providing more charge transfer.

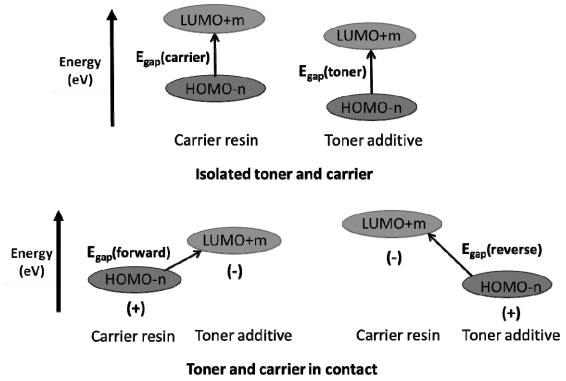

Figure 1. *Frontier molecular orbitals for toner and carrier separated and in contact in the formation of the charge transfer complex.*

Fig. 2 shows the precursor charge transfer complex of PMMA with silica, the HOMO donor is located on a carbonyl group of PMMA, the acceptor on a silanol OH group in the silica.

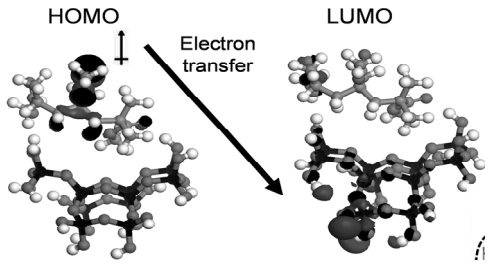

Figure 2. *HOMO donor and LUMO acceptor molecular orbitals for the PMMA/silica charge transfer complex. PMMA is at the top, silica at the bottom.*

Molecular mechanics (MM) was applied to find models for the most probable water adsorption sites for the isolated silica and isolated PMMA. Fig. 3 classifies the different water adsorption modes found. QM was then used to calculate the local energy minima for different adsorption modes.

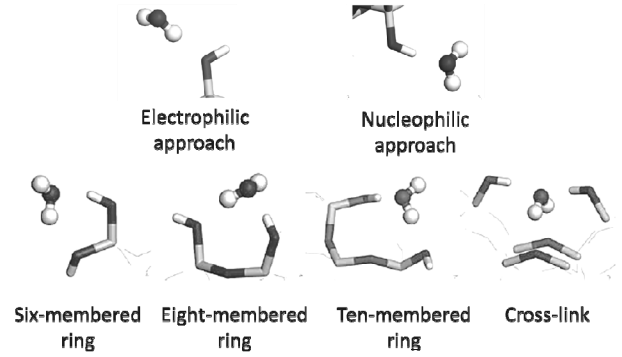

Figure 3. *Water adsorption modes found by molecular mechanics.*

It was previously shown [8] that the HOMO and LUMO of the isolated clusters, prior to forming a complex, are a good approximation to the HOMO and LUMO in the charge precursor complex. Thus, from the studies of water adsorption on the isolated complexes (not discussed here), modes of water adsorption were chosen that potentially affect the HOMO and LUMO, and these modes were then studied in the PMMA/silica charge precursor complex, using the same methods used for the isolated molecules. The three modes of water adsorption studied in the PMMA/silica complexes are shown in Fig. 4. The blocking mode is when water is sandwiched between PMMA and silica; capping is water adsorbed on the PMMA carbonyl oxygen that is the HOMO location; and adsorbing when water is adsorbed on the silica silanol that is the LUMO location.

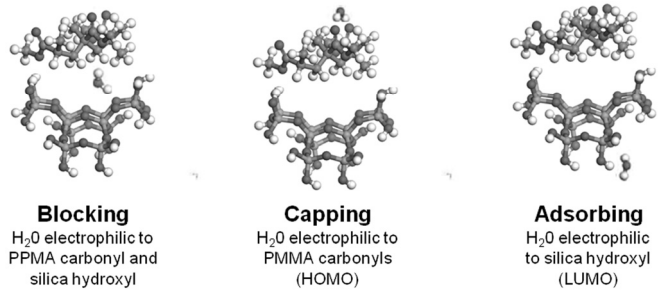

Figure 3. *Water adsorption modes studied in PMMA/silica complexes, PMMA is on the top, silica on the bottom.*

In total 7 different configurations, with a single water molecule in the complex, were modeled: two blocking, one capping and four adsorbing configurations. For the blocking case, there were two modes of water approach, electrophilic and nucleophilic to PMMA. Fig. 4. shows the resulting influence on the HOMO and LUMO for the electrophilic approach to PMMA. Although the water is located away from the HOMO on PMMA, it induces the HOMO to "move" toward the water molecule, as can be seen in comparison to Fig. 2 without water. In the LUMO the effect is less dramatic, but again there is an induction of the LUMO away from the silanol on silica toward the water molecule.

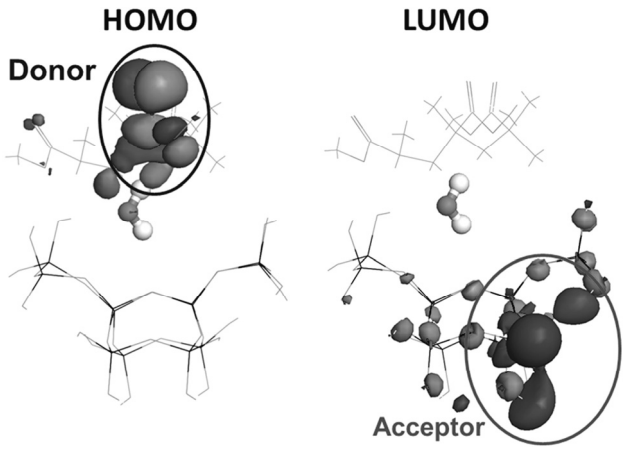

Figure 4. *HOMO and LUMO for electrophilic approach of water to PMMA with carbonyl orientated away from the interface. Top is PMMA, bottom is silica.*

Fig. 5 shows a portion of the energy level diagram for this blocking orientation of water, with as a reference a model where the water approach is to a silanol well way from the LUMO and HOMO, and thus showed minimal distortion of the HOMO and LUMO without water in Fig. 2. Note Fig. 2 cannot be used as a reference state for energy, since the inclusion of water changes the total energy of the system. As can be seen, in Fig. 5, the presence of the blocking water results in additional delocalization of the LUMO and HOMO (and the HOMO-1), which stabilizes both orbitals, lowering their energy. Since the effect here is greatest on the HOMO, the result is that the charge donation from PMMA to silica has a larger barrier, which results in less charge transfer.

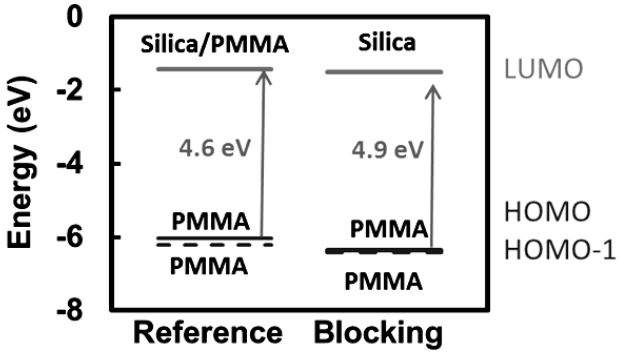

Figure 5. *Energy level diagram for reference state with non-perturbing water and with blocking water as shown in Fig. 4.*

There was one capping orientation studied, with water orientated electrophilic to the PMMA carbonyl on which the LUMO is located, as shown in Fig. 6. The effect of the water is dramatic on the HOMO, which is now located on the water instead of on the PMMA carbonyl. The LUMO is little affected.

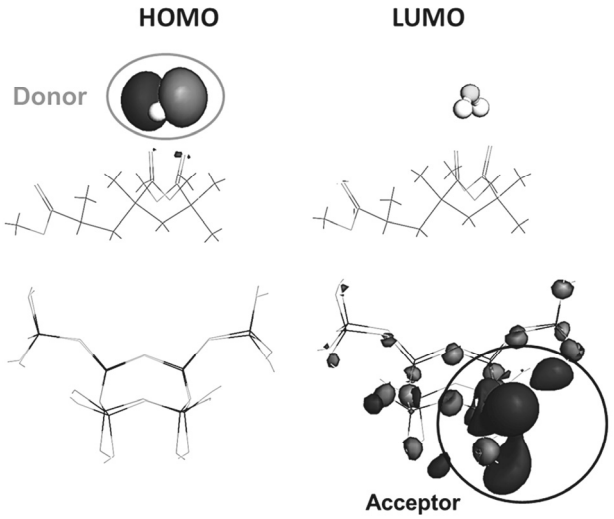

Figure 6. *HOMO and LUMO with "capping" electrophilic approaching water to PMMA carbonyl. Top is PMMA, bottom is silica.*

Fig. 7 shows the energy level diagram corresponding to Fig. 6. The HOMO-1 is the highest energy donor orbital that actually is at least partially located on the PMMA (along with water). Thus for the transfer from PMMA to silica the energy gap has widened due to the stabilization, reducing charge transfer. The HOMO on water though can also donate electrons to silica providing the required charge transfer, and it is of higher energy with a more favorable transfer gap. While this could help charge transfer, the result of such a charge transfer would be positive charge on the mobile water, which would likely be a mode of charge dissipation—thus the net effect of the water would likely be to reduce the overall net charge.

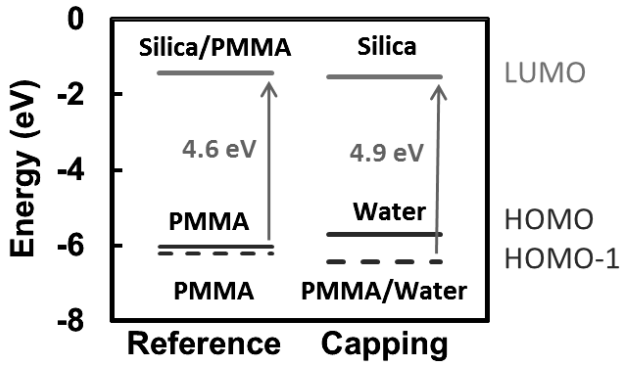

Figure 7. *Energy level diagram for water "capping" PMMA.*

There were four adsorbing modes of water studied, a nucleophilic approach to the silanol OH group LUMO site, two six-membered rings, and one eight membered ring (electrophilic to the LUMO), the latter shown in Fig. 8. Compared to Fig. 3 there is little disturbance to the LUMO orbital, aside from some delocalization of the orbital onto the water.

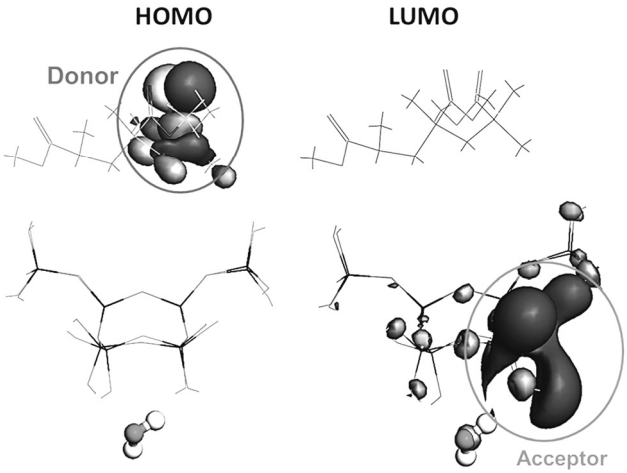

Figure 8. *HOMO and LUMO for water in "adsorbing" approach in 8-membered ring to silanol LUMO.*

Fig. 9 shows the corresponding energy level diagram for the "adsorbing" approach in Fig. 8. The result in this case is a stabilization of the LUMO due to the delocalization, resulting in a lower transfer gap, with the HOMO unaffected. Thus, in the interaction of water with the LUMO in this case the effect on the charge is actually apparently favorable.

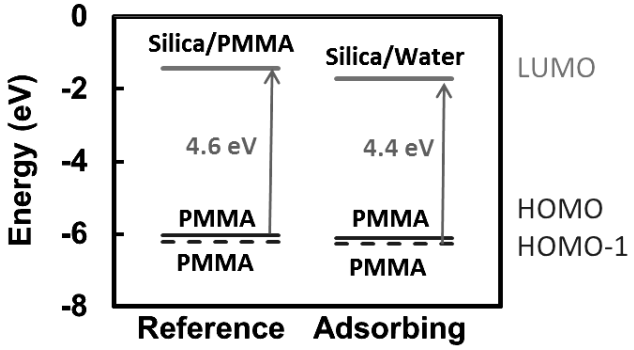

Figure 9. *Energy level diagram corresponding to Fig. 8 for water "adsorbing".*

Given the potentially different effects of the water approach on the LUMO and the HOMO, two different configurations were tested for the approach of two water molecules to the PMMA/silica complex. In both cases one water molecule approached the PMMA HOMO in an electrophilic approach, while one water molecule in an electrophilic approach to two silica silanols in a six-membered ring. The result in both cases was similar and is shown in Fig. 10. In this case the HOMO is on water and the LUMO also predominantly on water. Thus there is a direct charge dissipation path whereby the lowest energy process would cycle charge from water molecule to water molecule, from the HOMO to LUMO with little involvement of the PMMA or silica. This is effectively a conductive "wire" at the interface that would dissipate charge.

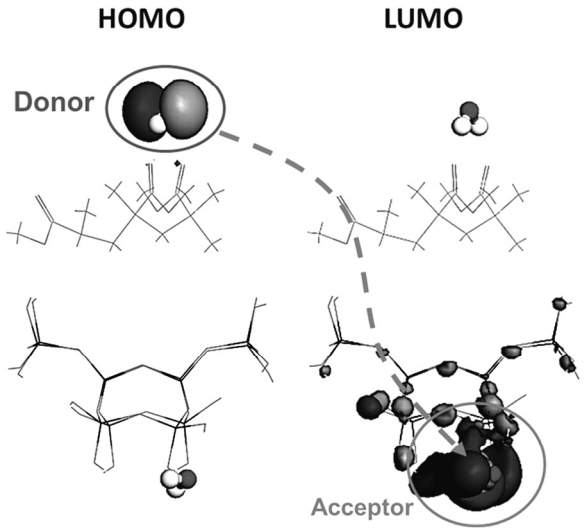

Figure 10. *PMMA/silica complex with two water molecules, one approaching the acceptor site one approaching the donor site.*

Fig. 11 shows the corresponding energy level diagram for two water molecules. The HOMO-1 has some electron density on PMMA, although some of the HOMO-1 is located on water. Thus some electron transfer can occur from the PMMA HOMO-1 to the silica LUMO. The gap is increased due to the greater stabilization of the HOMO by water, so the electron transfer is less favorable. Thus with two water molecules the electron transfer between PMMA and silica is less favored due to the larger energy gap, and also as there is a lower energy charge dissipation pathway.

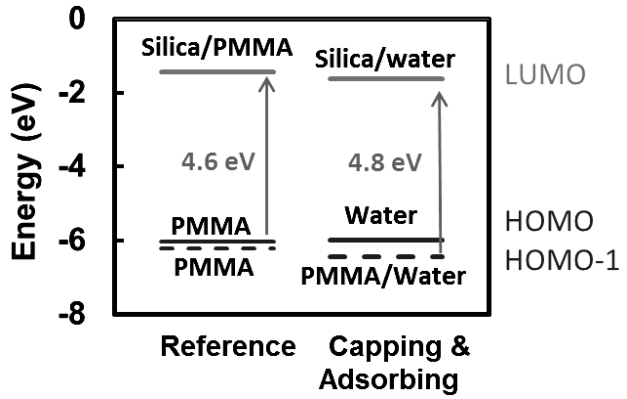

Figure 11. Energy level diagram for PMMA/silica complex with two water molecules.

Conclusions

MM and QM modeling has elucidated the effect of water on the frontier molecular orbitals and energy gaps for electron charge transfer for PMMA-silica complexes. The surface electronic properties are affected by water adsorption in a number of ways: water can induce electron density near its location, or can be part of a frontier molecular orbital for the complex, lowering the energy of that orbital. If water interacts with the HOMO it increases the charge transfer gap, with the LUMO it decreases the gap.

Four fundamental ways were found for water to affect charge transfer between PMMA or silica: 1) adsorption of water on the PMMA carbonyl decreases the energy of HOMO, increasing the charge transfer barrier; 2) water acts as part of the electron accepter when adsorbed at the active site of the silica LUMO, which lowers the LUMO and thus lowers the charge transfer barrier, but at the same time creates a charge dissipation pathway, as a part of the charge transfer is now to water, rather than to silica; 3) water acts as spacer between PMMA and silica, which increases the energy gap for charge transfer; and 4) water acts as a charge carrier, dissipating electrons by donating charge when adsorbed on PMMA, then accepting charge back when adsorbed on silica.

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Author Biography

Rick Veregin has Ph.D. in Chemistry from the University of Guelph in 1985. Since then has worked at Xerox Research Centre of Canada as a Senior Research Scientist, as a manager, and currently as a Principal Scientist, focused on the chemistry and physics of xerographic materials and integration into printing systems. Rick is an IS&T and ACS member, an IS&T Fellow, a recipient of the IS&T'S 2012 Carlson Award, and has 57 scientific publications and 129 US patents.