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First Principles Investigation of Quinizarin Chemisorbed on α-Al$_2$O$_3$

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Over the years the technique of persistent spectral hole-burning[1] has attracted much scientific attention.[1−5] The possible application to high-density optical storage devices[1,6] has driven a search for systems that exhibit persistent spectral hole-burning at higher temperatures.[5] Accordingly, the recent discovery[7−10] that several dye molecules show persistent spectral hole-burning up to the temperatures of liquid nitrogen when chemisorbed on alumina surfaces has caused much attention. In contrast, this effect disappears when the same molecules are dispersed in a matrix. Various hypotheses have been proposed to account for this behavior. In particular, whether the improved hole-burning properties are due to long-range effects induced by the surface has been discussed.[10] Specifically, this seems experimentally plausible[10,11] for quinizarin (1,4-dihydroxyanthraquinone) on γ-Al$_2$O$_3$ because a characteristic 40 nm red shift in the electronic spectrum is observed when the molecule is chemisorbed.[9] This effect has been taken as an indication of surface-induced modifications of the molecule's electronic structure.[10] This idea has been theoretically pursued by modeling of the surface as a cluster of atoms.[11] The cluster approximation, however, excludes by construction any possibly crucial long-range effects. Here, we transcend this kind of approach by performing *ab initio* calculations where we treat the molecule and the periodic surface on the same footing. As a result of our calculations we confirm the experimental strong red shift of the excitation energy upon chemisorption. However, we find that the main features of the molecule's electronic structure remain essentially unchanged by chemisorption.

The electronic structure calculations are based on Kohn−Sham density functional theory[12] in the local density approximation[13] augmented with exchange gradient corrections.[14] The core electrons are represented by supersoft pseudopotentials,[15] whereas the valence orbitals are expanded in plane waves with a highest kinetic energy of 25 Ry. The "direct inversion in the iterative subspace" (DIIS) method in conjunction with a preconditioning scheme is used for the electronic structure optimizations.[16] The combination[17] of a quasi-Newton technique and the DIIS method allows efficient geometry optimizations. The Car−Parrinello *ab initio* molecular dynamics simulations[18] (for reviews see ref 19) were done at roughly 300 K using a time step of 6 au (0.145 fs) with a fictitious electron mass of 1100 au; the length of the run was 145 fs.

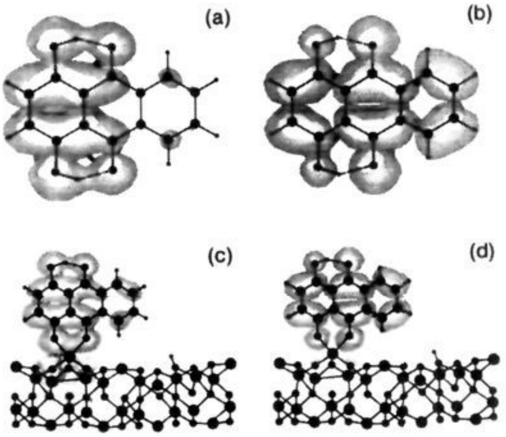

Figure 1. Optimized structures of isolated quinizarin (a,b) and quinizarin chemisorbed on the (0001) surface of α-Al$_2$O$_3$ (c,d) with the corresponding Kohn−Sham HOMO (a,c) and LUMO (b,d) superimposed on the left and right sides, respectively; all atoms included in the calculation are shown without any periodic images. Symbol sizes increase in the following order: hydrogen, oxygen, carbon, aluminum.

Since the structure of γ-Al$_2$O$_3$ depends sensitively on the conditions of preparation, we performed our calculations on the much better characterized α-Al$_2$O$_3$. We investigate the basal-plane (0001) surface of α-Al$_2$O$_3$ (corundum), which is terminated by a layer of aluminum atoms; our calculated lattice constant 5.159 Å for the rhombohedral unit cell of bulk α-Al$_2$O$_3$ overestimates the experimental value[20] by only 0.6%. The (x,y,z) extensions of the periodically replicated orthorhombic box are (4.789, 16.589, 17.286) Å and accommodate two unit cells in the y-direction of the surface cut. The surface in slab geometry consists of 60 atoms in nine atomic layers (Al−O−Al−Al−O−Al−Al−O−Al) along the z-direction. The pronounced surface relaxation as reported in recent calculations (−86% for the distance of the two outermost layers[21,22]) is very well reproduced (−81%) with Γ-point sampling. All atoms, including the surface atoms, were fully relaxed in all our calculations, and no symmetry constraints were imposed. The compound system consisting of the chemisorbed quinizarin in the yz-plane is depicted in Figure 1c; the remaining hydrogen atom of quinizarin is deposited on the surface sufficiently far from the bonding site.

The exchange gradient corrected density functional[13,14] used yields for an isolated quinizarin molecule a dipole moment of 2.4 D, which is in very good agreement with the experimental value,[23] 2.46 D. The calculated intramolecular hydrogen bond length of about 1.7 Å differs somewhat from the experimental value,[24] 1.77 Å. However, this deviation is acceptable in view

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of the flatness of the potential energy surface for such bonds. The Kohn–Sham HOMO–LUMO gap of roughly 1.9 eV underestimates the experimental value,[9] 2.42 eV. This is not unexpected as it is well-known that the local density approximation in general underestimates such gaps, whereas it describes qualitative changes and trends reliably. The final results of geometry optimizations of the isolated molecule and of the compound system are shown in Figure 1, parts a and c, respectively. First of all we find that the molecule stays perpendicular on the surface. This allows the formation of a chelate bond between two neighboring oxygen atoms of quinizarin and a surface aluminum atom. Interestingly, the complexed aluminum atom is pulled out of the surface leading to a zero-dimensional surface reconstruction. This results in a 5-fold-coordinated aluminum atom, which is along the lines of earlier semiempirical cluster calculations.[11] Thus, the molecule is not simply adsorbed on the planar surface, but instead the surface is locally strongly deformed by chemical bonding. This suggests that in real samples the molecules are preferentially located at surface defects where one aluminum atom is in an exposed position after removal of the usually present surface hydroxyl groups.

Starting from the optimized structure (Figure 1c) we performed a short Car–Parrinello molecular dynamics run at room temperature in order to check the stability of this structure. Only small amplitude vibrations of the atoms around their equilibrium positions were observed, without any indication of a systematic motion of the molecule away from the initial configuration (Figure 1c) during the time of the run. In addition, we find that the electronic structure after the run is very similar to that of the reported minimum structure (Figure 1c). Thus, we confirm that the perpendicular arrangement (Figure 1c) is at least a quite stable local minimum, and that the chelate bond is much stronger than an alternative interaction between the π-system and the surface.

Previous PM3/MRD-CI calculations[11] have shown that the $\pi \rightarrow \pi^*$ transition to the first excited state, which is relevant for the hole-burning process, is described to a very good approximation by a simple excitation of one electron from the HOMO to the LUMO. Thus, we have studied the Kohn–Sham HOMO and LUMO of the isolated and chemisorbed molecules; see Figure 1a,b and Figure 1c,d, respectively. While quantitatively the Kohn–Sham orbitals are not expected to be accurate, they are known to reproduce reliably most qualitative features of the electronic levels. It can be seen from Figure 1 that the frontier orbitals remain essentially localized on the molecule with almost no charge density on the surface, and that the pronounced charge transfer character of isolated quinizarin is preserved in the chemisorbed situation. In spite of this, the excitation energy of quinizarin, i.e., the difference between the Kohn–Sham HOMO and LUMO energies, is shifted to the red by 0.36 eV upon chemisorption. This agrees qualitatively with the experimentally observed red shift[9] of 0.17 or 0.19 eV depending on whether the chemisorbate was measured in vacuum or with methylene chloride as solvent; the molecule was measured in methylene chloride.

In addition to these calculations we investigated quinizarin in a cluster geometry with a single aluminum atom attached in the chelate position.[25] Starting the geometry optimization with two hydroxyl groups and two water molecules complexing the aluminum atom we observe that one water molecule is expelled and forms a hydrogen bond to the other water molecule. The frontier orbitals are strikingly similar to the ones shown for chemisorbed quinizarin (Figure c,d), which confirms the assumption[26] that the character of the $\pi \rightarrow \pi^*$ transition in quinizarin is conserved upon complexation with trivalent metal cations. The excitation energy of roughly 1.6 eV is again red shifted by about 0.36 eV relative to the isolated molecule. Thus, the red shift in our surface calculation is of a magnitude similar to that in our cluster geometry. Long-range surface effects seem to be of minor importance for the properties of the electronic excitation of the chemisorbed molecule.

In summary, we have shown by *ab initio* calculations that quinizarin chemisorbed on the (0001) surface of α-Al_2O_3 stays perpendicular on the surface and forms preferably chelate bonds with surface aluminum atoms at exposed sites. Comparing the electronic structure of isolated quinizarin, surface chemisorbed quinizarin, and quinizarin complexed with a cluster of one hydrated aluminum atom, our results suggest that the improved spectral hole-burning properties of chemisorbed quinizarin cannot be explained in terms of a change of the electronic characteristics due to long-range surface effects.

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