

SURFACE REACTIONS IN PHOTOELECTROCHEMICAL CELLS

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ABSTRACT: The fast electron transfer between the Ru metal complex- or organic dye-based photosensitisers in a photoelectrochemical solar cell, and the semiconductor electrode (typically TiO₂ in the form of anatase) is investigated by use of quantum chemical calculations. A coumarin-derivative dye plus a chunk of an anatase electrode is included in the model. Optimisation reveals the most favourable anchoring of the dye molecule, which has not previously been determined. The mechanism of the fast transfer is confirmed to involve a collective excitation involving both centre and ligand atoms in the dye molecule.

1 INTRODUCTION

Photoelectrochemical cells can be used for solar electricity and hydrogen production, computer displays and 3-dimensional data storage. Understanding the ultra-fast ($\approx 10^{-15}$ -second) electron transfer from a light-absorbing dye to the adjacent semiconductor nanoparticles, which constitute the negative electrode, requires the study of both the dye molecule and its surroundings, typically an anatase semiconductor surface to which it adheres, and an electrolyte replenishing transferred electrons from the positive electrode. Earlier work has established the strongly collective nature of the dye excitation under solar irradiation [1] and the modest influence of the electrolyte on the excitation process [2]. The present work goes on to include both the dye particle and the semiconductor surface, to which it adheres, in order to be able to describe the entire electron transfer process.

Experimental efforts to establish a structural description of the attachment of photo-sensitiser dyes to an anatase surface have proven inconclusive [3]. The spectroscopic methods have left so many interpretations that neither the precise atoms of close contact between dye and the underlying surface, nor the distance and angles of the dye relative to the anatase surface can be inferred. The present work therefore embarks on a quantum chemical optimisation of the dye plus a chunk of surface atoms, using Hartree-Fock and density functional theory [4]. Such calculations have proven successful in explaining the action of simple catalysts (e.g. Pt) in ionising hydrogen or oxygen molecules [5]. The present calculation, including a representative piece of the TiO₂ semiconductor surface together with a large coumarin-derivative dye molecule [6] of some 50 atoms, is at the limits of current computer power, and each optimisation run represents about a month of continuous CPU time on a currently state-of-the-art PC. The structure of the molecules involved is shown in Fig. 1, before optimisation of their relative positions.

2 OPTIMISATION CALCULATIONS

The optimisation is done in two steps, using quantum mechanical calculations. The structure in the ground state and the excited states of the coumarin-derivative molecule was determined by density functional theory optimisation (using the potential form called B3LYP) and a cor-

responding time-dependent calculation for excitations [8,9]. Detailed assumptions may be found in refs. [1,2]. The TiO₂ structure is taken to be known. Then, the internal structure of both the dye molecule and the anatase lattice are kept fixed, while the minimum energy is sought as function of the dye distance to the surface, the angle of inclination and rotation of the dye relative to the main lattice directions. Secondly, all atoms in the dye and the top layer of the surface are left free to be repositioned in a full scale optimisation of the total energy. The results are shown in Fig. 2 and 3, for the single layer anatase included in the initial calculation. It exhibits a considerable distortion of both dye structure and anatase surface, relative to their structures in isolation. The ligand “arm” stretching out from the modified coumarin molecule is bent and rotated with respect to the rest of the molecule, so that a closer contact with the underlying surface atoms becomes possible. Also the surface layer of the anatase lattice is distorted in such a way, that the adherence of the dye molecule is eased.

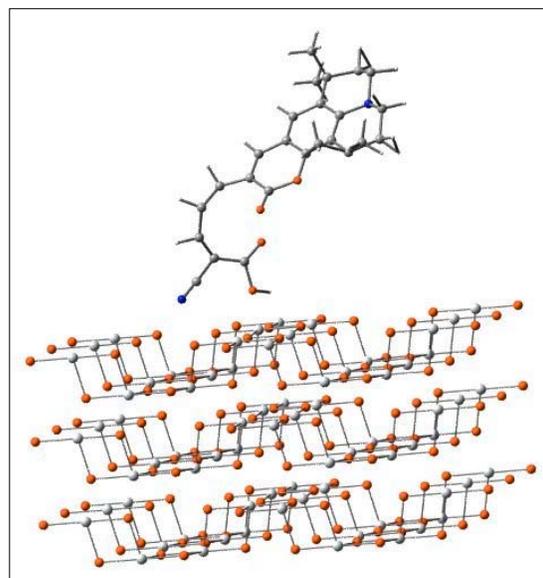


Figure 1: Chunk of anatase with coumarin-derivative dye molecule. The relative positions represent the arbitrarily chosen starting point for optimisation.

The distortion of the anatase structure facing away from the dye molecule is not realistic, because the semiconductor stretches many unit cell lengths both in the

two directions along the surface, and down below the surface. Therefore, a more detailed constrained optimisation was performed, now using two layers of TiO_2 but keeping the bottom and end atoms at fixed positions, simulating the action of the extended semiconductor structure.

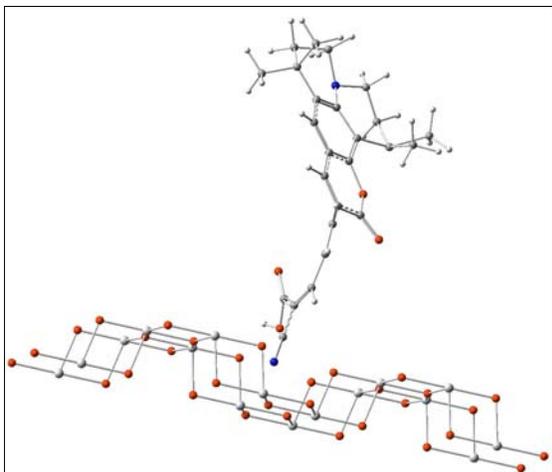


Figure 2: Simplified model used for initial exploration, with only one layer of anatase. The distance and orientation of the coumarin-derivative molecule relative to the surface has been loosely optimised, without change in the internal co-ordinates of the two molecules. This configuration is then used for the full optimisation shown in Fig. 3 [4].

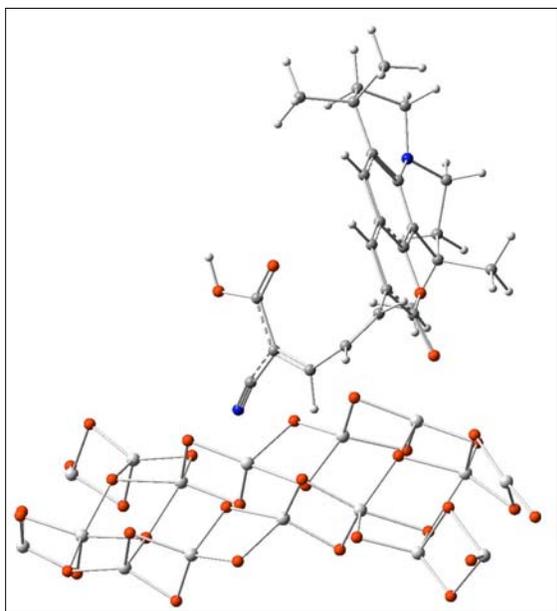


Figure 3: Result of applying unrestricted optimisation of the position of all atoms to the simplified structure of Fig. 2. Note that the arm of the coumarin molecule is rotated relative to Fig. 2, and the anatase surface is distorted. The combination greatly increases electron wave function overlap, but is unrealistic in its distortion of the anatase structure [4].

The results of this realistically restricted optimisation starting from the configuration shown in Fig. 4 are pre-

sented in Fig. 5. First of all, it is seen that the anatase surface is now very little changed by optimisation, as one would expect. The changes that do occur are fractions of a nanometer displacements of the atoms directly under the coumarin-derivative molecule.

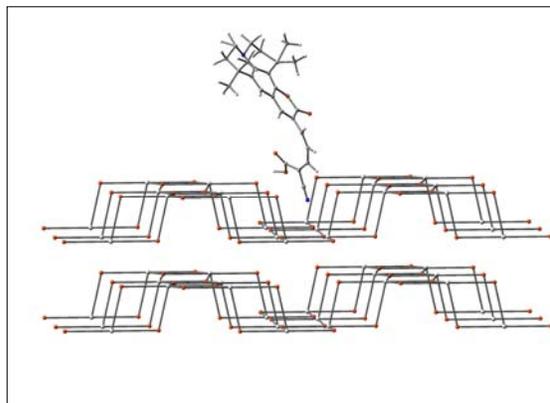


Figure 4: Initial structure used for the final, restricted optimisation. The coumarin-derivative molecule is positioned in accordance with the preliminary optimisation from Figs. 2 to 3 [7].

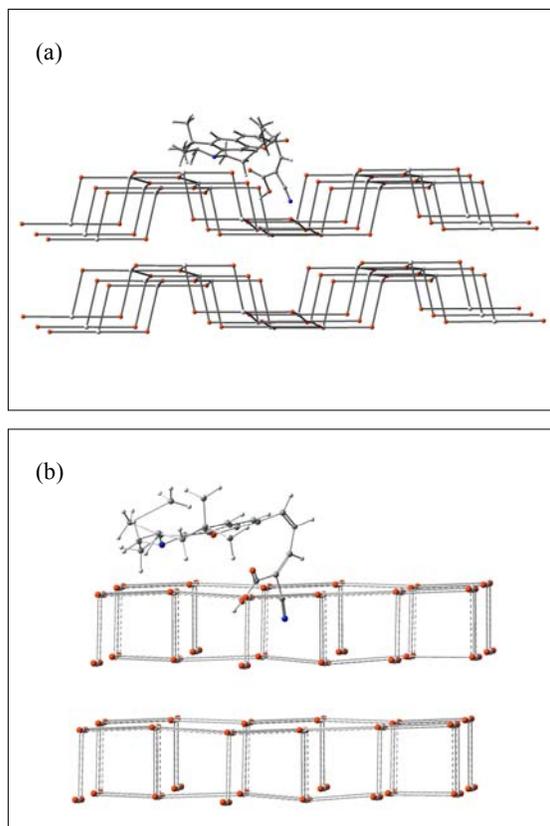


Figure 5: Final results of realistically restricted optimisation. (a): seen from the same angle as Fig. 4 and (b): seen from the “end” of the anatase wavy lines connecting atoms in (a) [7].

The “arm” of the coumarin-derivative molecule is seen to penetrate the anatase structure down to the space between the first and second atomic layer, at a location where the structure is open enough to allow this. Fur-

thermore, the other end of the molecule, the one that contains the simple coumarin structure, is bending down towards the anatase surface. This was not expected, but speculations on a similar two-point attachment has been made for some of the ruthenium-based dyes. The advantage of doing this becomes clear when one realises, that the electron transfer from dye to semiconductor is not a simple transition from one atom to another. If the transfer involved only an excitation of one atom in the coumarin-derivative ligand "arm", only this atom would have to be close to the anatase surface. But because the excitation is collective, as demonstrated in refs. [1,2], some of the transfer may involve parts of the electron density in the central part of the coumarin molecule, and therefore it becomes energetically favourable to have also this part move closer to the receiving semiconductor surface.

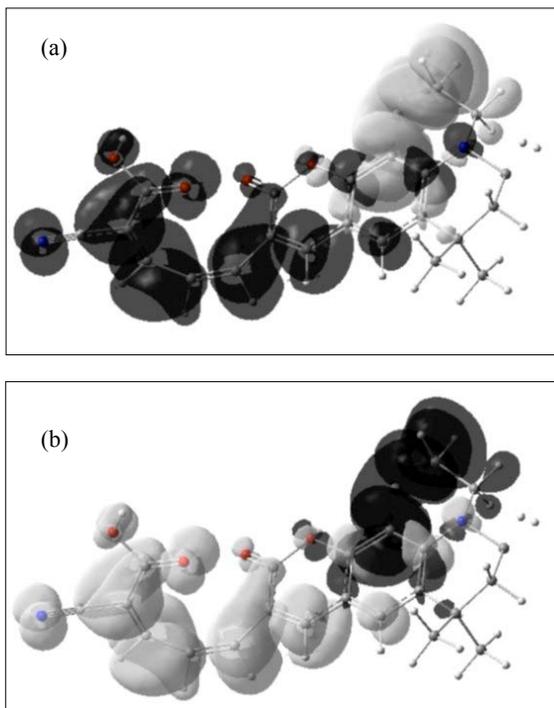


Figure 6: Electron density difference between excited and ground state of coumarin-derivative dye. Positive values are darkened at top (a), while negative values are darkened at bottom (b). The calculation further explained in [2] uses the density functional theory B3LYP [4].

That this is so can be seen from the electron density difference between the first photo-excited state of the coumarin-derivative dye (the one excited by receiving a solar photon) and the ground state, as illustrated in Fig. 6. The excitation removes electron density from a large part of the central coumarin area and transfers it to all the atoms along the ligand arm of the derivative molecule.

3 CONCLUDING REMARKS

The type of optimisation work performed here, and the understanding obtained, may have several practical applications in selecting dyes and nano-particle deposition structure for obtaining high efficiency of solar conversion in photoelectrochemical dye-based cells.

4 REFERENCES

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5 APPENDIX: COMPUTATIONAL ISSUES

As an illustration of the importance of including two-electron correlations and the effect of the exclusion principle in the calculations, Figs. 7-9 show a number of simplified calculations of the electronic density difference between the lowest excited state and the ground state of the coumarin derivative dye molecule. Fig. 7 shows a semiempirical ZINDO calculation including only 10 molecular orbitals on each side of the Fermi level. Fig. 8 shows the same for a Hartree-Fock calculation without electron-electron correlations. Fig. 9 shows the density difference between the lowest unoccupied and the highest occupied molecular orbital from the B3LYP calculation.

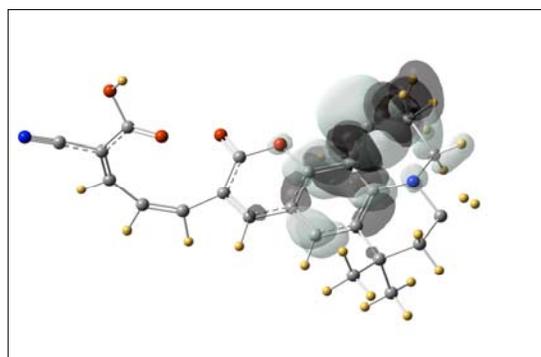


Figure 7. Electron density difference between first excited and ground states, calculated for the coumarin-based dye molecule using the ZINDO approximation.

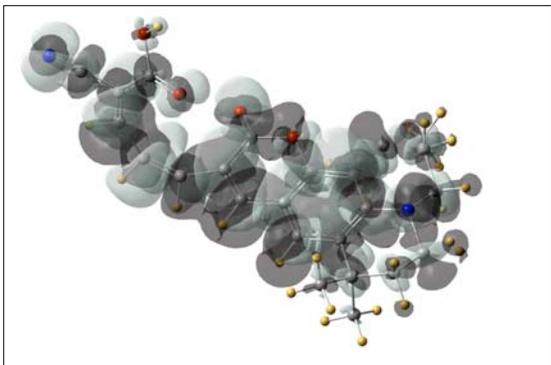


Figure 8. Electron density difference between first excited and ground states, calculated for the coumarin-based dye molecule using a Hartree-Fock calculation. The shading in Figs. 7-10 represents density iso-curves at a value of 0.0004, with dark shading indicating larger density in the excited state, and light shading larger density in the ground state.

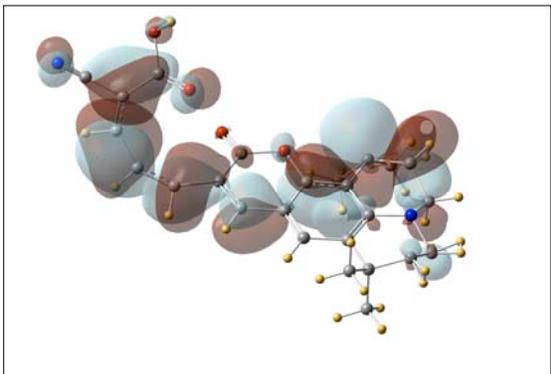


Figure 9. Electron density difference between first excited and ground states, calculated as the difference between LUMO and HOMO densities from the same B3LYP calculation as Figs. 6 and 10.

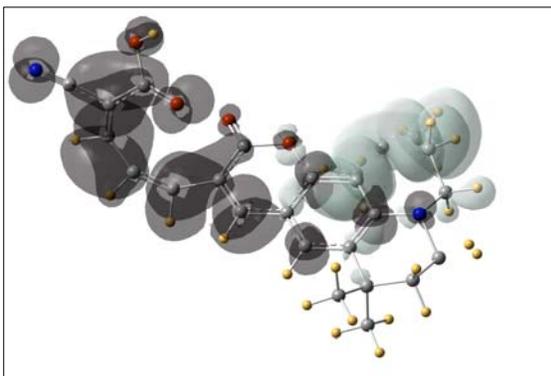


Figure 10. Electron density difference between first excited and ground states, calculated using the density functional theory B3LYP method as in Figs. 6, and a large orbital basis called 6-311+G(d,p).

Comparing Figs. 9 and 10 one sees that although the molecular orbitals from the full calculation gives a qualitatively correct picture of the transition of the electron wave function to the periphery of the molecule, the

time-dependent diagonalisation provides a much more plausible picture without the appearance of areas of both signs for the density difference in all parts of the molecule as in Fig. 9 (a feature caused by the simplicity of using differences between orbitals which themselves contain general correlations but do not take into account the specific correlations responsible for the structure of the excited state). The ZINDO calculation predicts an excitation energy that is realistic, but the wave functions are totally incorrect. The Hartree-Fock calculation is unable to produce a realistic excitation energy and the density difference is therefore not plausible. Only the full calculation using density functional theory and a sufficiently large basis of Gaussian functions is producing a plausible explanation for the observed feature of an excited state allowing the electron to jump to the anatase surface with a large transition probability.