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UNDERSTANDING PHOTOELECTROCHEMICAL SOLAR CELLS

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ABSTRACT: The paper describes the layout of photoelectrochemical (PEC) solar cells and discusses key features. In particular, the nature of the dye excitation by which sunlight initiates the electron transfer processes is investigated by *ab initio* quantum chemical modelling. It is suggested that the dye excitation process and the following rapid electron transfer to a semiconductor surface is a collective phenomenon involving a large number of dye electrons. The prospects for replacing experimental trial and error by model-based choice and optimisation of materials are briefly discussed.
Keywords: organic solar cell, dye-sensitised, modelling

1 PEC CELL STRUCTURE

A common layout of PEC solar cells is shown in Fig. 1. It is instructive to discuss it in comparison with conventional photovoltaic (PV) solar cells.

In the PEC cell, solar light absorption takes place in a two-dimensional layer of a dye sensitiser, while the transport of electrons takes place in separate sections of the cell (the semiconductor to the left in Fig. 1 and the electrolyte to the right). Thus for example, the semi-

Figure 1: Layout of PEC solar cell with indication of energy levels (E_f is the Fermi level of the semiconductor material)
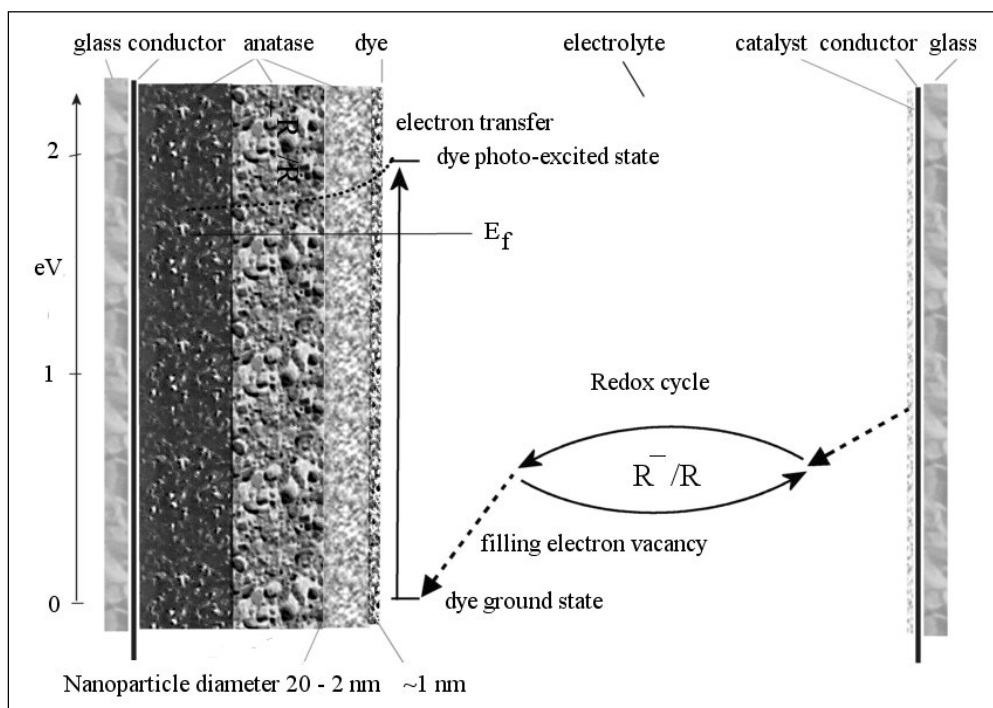
A PV solar cell device consists of n- and p-doped semiconductor materials forming a p-n junction. The materials are chosen in such a way, that the band gap of the semiconductor allows absorption of light from most of the solar spectrum. In the dark, an equilibrium without any current is formed by the junction. Under irradiation, absorption of light takes place over the entire volume of the cell, and subsequently the excited electrons and hole vacancies can travel across the device and form an electric current in an external circuit. A disadvantage is that the semiconductors act both as light absorbers and as electron transfer media, thus making it difficult to optimise materials for both functions. Typically, with the electron band structure suited for solar light absorption, there will be several recombination processes competing with the transport of electrons to or from electrodes [1].

conductor can be optimised for electron transport, with an energy gap that is high enough to minimise direct absorption and reduce bulk recombination. The use of sensitisers capable of absorbing light with high efficiency was first suggested by James Moser in 1887 [2], by analogy to photographic emulsions.

The light absorption in a single two-dimensional layer long restricted the efficiency of solar conversion by such devices to levels below 10^{-4}. The crucial advance was made in 1976, when Tsubomura *et al.* [3] used nanostructured semiconductor material upon which the sensitiser dye could adhere. The effective surface area of dye exposed to solar radiation is in this way brought up to the order of 1000 times the geometrical surface. As indicated in Fig. 1, several layers of nanostructured semiconductor material are used. The one closest to the conductor (usually glass with a conductive coating) must

be solid, in order to avoid that the electrolyte reaches the anode conductor. But subsequent layers consist of nodules of diminishing size (from 20nm down to a few nm) and density, but in contact so that the electron transport is not hindered. These features are demonstrated by tunneling electron microscopy. The larger nodules are roughly spherical, while the smaller ones may be more irregular. The material presently used for the anode nano-particles is TiO_2 in the form of anatase (Fig. 2). Compared to the other forms of titanium oxide (rutile and brookite), anatase better accommodates the dye molecules and form nodules rather than flakes. The large-side dimension of the unit cell shown in Fig. 2 is about 0.2nm.
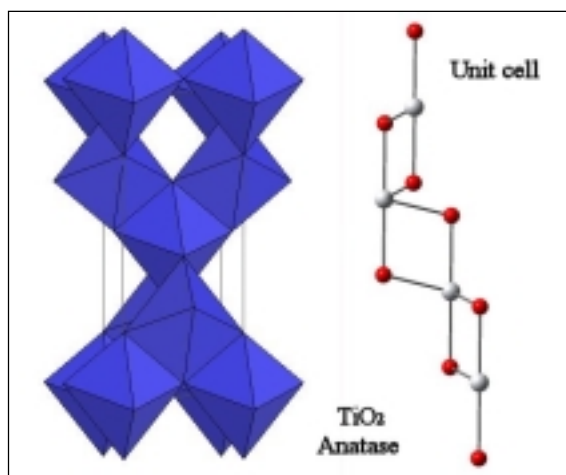

Figure 2: Anatase structure [4] and unit cell.

Several other semiconductor materials have been investigated, but so far anatase has shown the best overall properties (function and preparation) and is used fairly universally [5]. Electron transport through the anatase layers follows conventional solid state physics, except for the issue of nodule coherence. A simple modelling effort has successfully described the transport as random walk, rather than governed by hopping models [22].

On the cathode side, a redox couple is used to supply the electron to replace the one being excited in the dye and transferred to the anatase before it decays back to the dye ground state. The electrolyte is typically acetonitrile (C_2H_3N), and the redox couple iodine/tri-iodine (I^-/I^-_3), which has been used rather exclusively since the first application by [3]. This does not seem ideal, as the difference between the anatase Fermi level and the I^-/I^-_3 chemical potential, which determines the cell open circuit voltage, is only about 0.9eV, as compared with typical dye excitation energies of 1.8eV. Many efforts have been directed at finding more appropriate redox shuttle systems, but so far none have shown overall properties making them preferable to the I^-/I^-_3 couple [6]. Electrolyte and redox couple integrity and lifetimes are of concern. A comparison to batteries is appropriate, and battery lifetimes are rarely as long as desired for solar cells that may be incorporated directly into building components and structures.

A further energy loss takes place at the cathode, where application of a catalyst is required in order to obtain the desired rate of electron transfer from electrode to electrolyte. As in batteries and fuel cells, traditionally preferred catalysts are based on platinum, but alternatives

are under investigation. Generally speaking, the use of liquid electrolytes and catalysts is undesirable, and the much slower electron transfer through the electrolyte and its redox couple (as compared with the semiconductor transport) is likely to be the overall limiting factor for current in the device. However, the reason for this choice is obvious: The cell is produced by deposition of anatase layers on the anode and subsequent annealing, processes taking place at several hundreds of degrees celcius. The dye is then applied, either by a soaking or a flushing process, creating the huge intrinsic surface for solar collection. Typical dye melting points are 80-100°C, so applying a second semiconductor material (if one with appropriate properties could be found) from the other side at appropriate temperatures would destroy the cell. More gentle application not requiring high temperatures is not likely to allow the surface contact area between dye and semiconductor to be equally large on both sides.

An alternative would be to find another material not requiring high temperatures for penetrating into the cavity structure of the initial semiconductor plus dye layers. Possible candidates would be conducting polymers or the ion-carrying polymers used in fuel cells. Actual achievements of 2-3% energy conversion efficiency have been obtained with two types of polymer system. One uses a gel network polymer as electrolyte [7]. The other is a type of plastic solar cell, where the already known ability of ^{60}C-molecules to absorb solar radiation [8] is used to create a fairly large absorption area of ^{60}C sensitiser imbedded in a suitable polymer [9].

The discussion of sensitiser choice is the subject of the following section.

2 SENSITISER OPTIMISATION

The sensitiser requirements include
• high absorption capability over the range of spectral frequencies characteristic of sunlight
• energetically suitable excited states
• good attachment to semiconductor nanoparticles, that ensures rapid electron transfer (in competition with de-excitation and back-transfer from semiconductor surface to dye sensitiser)
• easily accepting replacement electron from electrolyte
• dye lifetime consistent with stipulated device life

The search for optimised sensitisers have usually focussed on a particular family of molecules. For example, the Grätzel/Lausanne group has looked at metal complexes, notably based on ruthenium polypyridines, meticulously synthesising one variant after the other, adding rings, thiocyanate ligands and carboxylate groups in different combinations. The size of the molecule, in combination with its excitation spectrum, determines the frequencies of solar radiation that can be absorbed, and the associated cross sections. The "black dye" (Ru, 3 pyridine rings, 3 thiocyanate ligands and 3 carboxylate groups) has led to the highest overall conversion efficiency, being 10% for laboratory cells (area about 10^{-4} m^2) [10]. For comparison, an efficiency of 5% is claimed for a large cell (of the order of 1 m^2) in industrial production [11].

An earlier favourite is the "N3 dye" (Ru, 2 bipyridine rings, 2 thiocyanate ligands and 4 carboxylate groups). It is particularly willing to transfer an excited electron to an

anatase surface, a fact that has been attributed to its attachment to the anatase surface by two carboxylate binding sites at approximately the same spacing as the "indents" in one anatase surface [12] (cf. Fig. 11). However, the light absorption stops below 800nm, implying smaller efficiency for many potential real-life collector sites. Fig. 3 compares spectral sensitivities of the two dyes mentioned above, plus the coumarin-derivative organic dye considered in the next section.
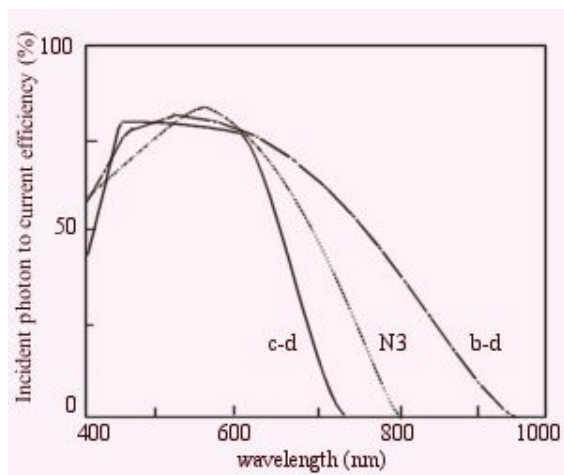

Figure 3: Spectral sensitivity (c-d: coumarin derivative, N3 and b-d (black dye) ruthenium complexes) [15,10]
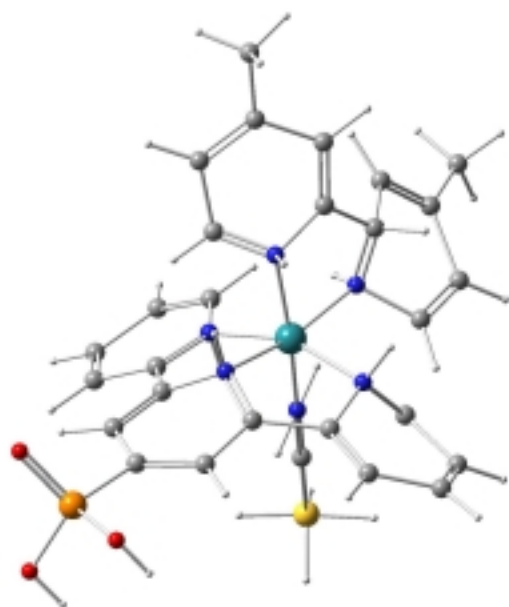

Figure 4: Calculated structure of phosphonated Ru-terpyridine sensitiser synthesised by [13] (a PO_3 group at bottom left, NCS-group bottom mid-behind)

Fig. 4 gives the molecular structure of a ruthenium dye in family with the "black dye" (2 pyridine rings replacing two thiocyanate ligands), but with a spectral sensitivity closer to the N3 dye [13]. The strongly 3-dimensional structure emerges from the *ab initio* Hartree-Fock optimisation modelling software Gaussian 98 [14], no matter whether the two-plane structure of [13] is used for initial parameters, or instead an already highly 3-dimensional structure based on heuristic rules (as

implemented in the companion software GaussView). The accuracy of such models will be discussed below.

3. MODEL CALCULATIONS

The structure of newly constructed sensitiser molecules is often roughly given by that of known components and general rules of thumb. However, the addition of new features which enhance solar absorption or helps electron transfer out of the molecule may give rise to structures not amenable to simple guesses, e,g. due to isomerism or for other reasons such as energy surfaces in configuration space with more than one minimum. From the point of view of quantum mechanical modelling of the molecular structure, this means that the outcome of an optimisation will depend on the starting shape. Built-in routines in software such as Gaussian-98 use a number of methods to find the deepest local minimum: After calculating gradients of the energy surface in different directions, the programme decides what algorithm to use, e.g. linear or quadratic extrapolation. Still the number of steps required for finding the minimum is large (typically 100-200), so that it is often necessary to perform the optimisation runs with a simpler model than later used for the detailed calculation of ground and excited state energies.
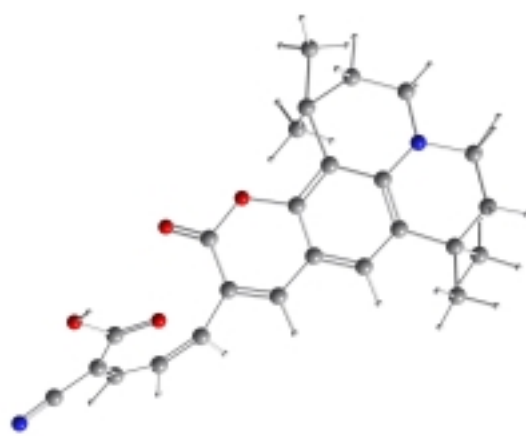

Figre 5: Optimised structure of coumarin-derivative organic dye synthesised by [15]
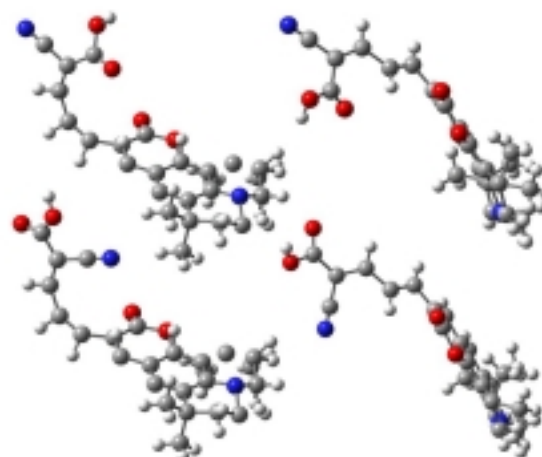

Figure 6: Four isomers of coumarin-derivative dye

Fig. 6 shows some identified isomers of the coumarin-derivative proposed by the Arakawa-group [15] and shown in Fig. 5. This sensitiser is used for the model calculation, because of the considerable interest in finding an organic sensitiser of reasonably high efficiency, that can replace the expensive ruthenium complexes.
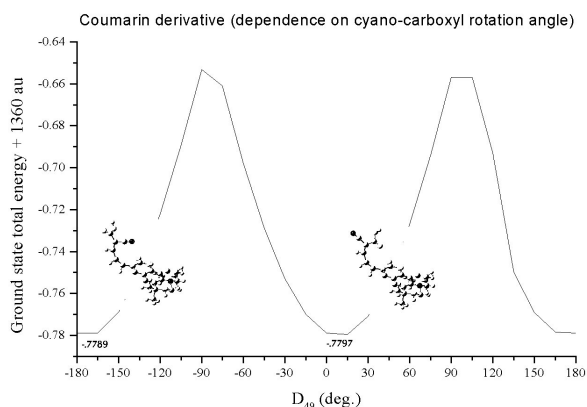

Figure 7: Energy as function of rotation angle for CN-CO$_2$H branching (left hand isomers of Fig. 6)
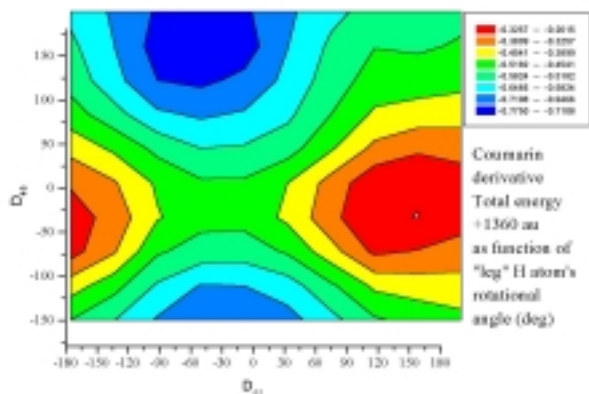

Figure 8: Energy as function of two hydrogen position angles along the "leg" of the molecule

The derivative in Fig. 5 is one of a series of molecules synthesised by the Japanese group. They chiefly differ in the layout of the "arm" stretching out from the well-known coumarin dye structure. The isomers indicated in Fig. 6 involve a rotation of the final CN and CO$_2$H branching, or of the position of hydrogen atoms in the three CH's of the "arm". Figs. 7 and 8 gives the results of specifically varying the angles defining the isomerism. It is seen (Fig. 8) that there is a clear energetic preference for the 3 hydrogen atoms to be on line, but that the end rotation (Fig. 7) exhibits two minima of nearly the same depth. Selecting the lowest one, the rest of the coordinates are now varied. Some handle on the accuracy of the optimisation can be obtained from spectral data (notably NMR), but in many cases the data are insufficient to determine the features fully. It is difficult to know, which RMS deviation should be allowed.

The optimisation calculations was using a simple set of 331 basis states (3-21G), while the final calculations used a larger basis set of 641 basis functions, including diffuse polarization functions (6-31+G(d)). The Schrödinger equation is solved under the assumptions:

• nuclear motion neglected

• Gaussian functions are used as basis: they are linear combinations of atomic wave functions

• the Hartree-Fock method is used to find a selfconsistent solution in terms of determinants of a set of "molecular orbits" (MO), which again are linear combinations of the Gaussian functions with coefficients to be determined.

• Hartree-Fock (HF) implies that each electron is moving in the mean field from all the other particles. This allows the best ground state wave function to be determined.

• higher electron correlations may be added, in order to get better predictions for energies, and to determine excited states, the calculation of which by time-dependent HF involves determining the lowest eigenvalues of a determinant. This can be carried to any order, approaching the exact solution to the Schrödinger equation.
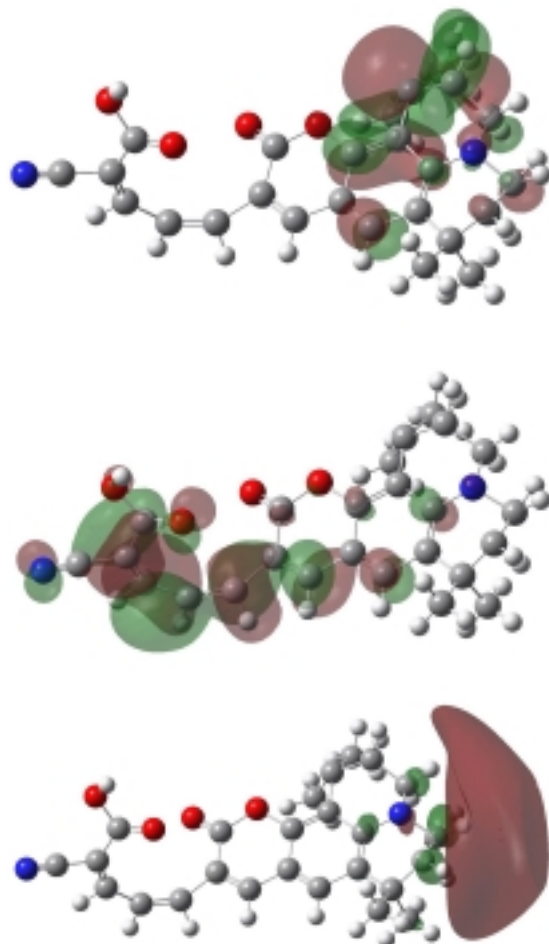
Figures 9: Electron density of HOMO (top), LUMO (middle) and 2nd unoccupied molecular orbital (bottom), based on selfconsistent field (SCF) calculation

Fig. 9 shows the molecular orbits near the Fermi level for the HF ground state calculation. It is seen that moving an electron from the highest occupied orbit (HOMO) to the lowest unoccupied one (LUMO) involves reducing the electron density in the coumarin-part of the molecule, and increasing it along and particularly at the end of the "arm" attached to the molecule. However, at this level of

approximation, the energy difference (LUMO minus HOMO) is still nearly 8eV, as opposed to an experimental value of 1.8eV]15]. The second unoccupied orbit (Fig. 9 bottom) is quite different in nature.

In order to estimate more realistically the energy of the first excited state of the coumarin-derivative dye molecule, a number of calculations have been performed. A first orientation may be obtained by simple semi-empirical methods like ZINDO-1 [16]. Using this with a basis of 10 molecular orbitals on each side of the Fermi level gives a lowest excited triplet (spin=1) state at 1.40eV and a second singlet (spin=0) state at 1.95eV. As the next step, one may use the *ab initio* ground state calculation and add various types of configuration interaction. The ground state is now calculated with a larger basis of 641 base functions forming 1096 gaussian functions, including polarisation and diffuse functions [14]. In the HF calculation, this lowers the ground state energy by some 215eV. A further improvement is including some lower order of configuration interaction in the energy calculation, by a density functional method [17] including exchange forces, as proposed by Becke and denoted B3LYP [18]. This brings the ground state energy down by a further 225eV.
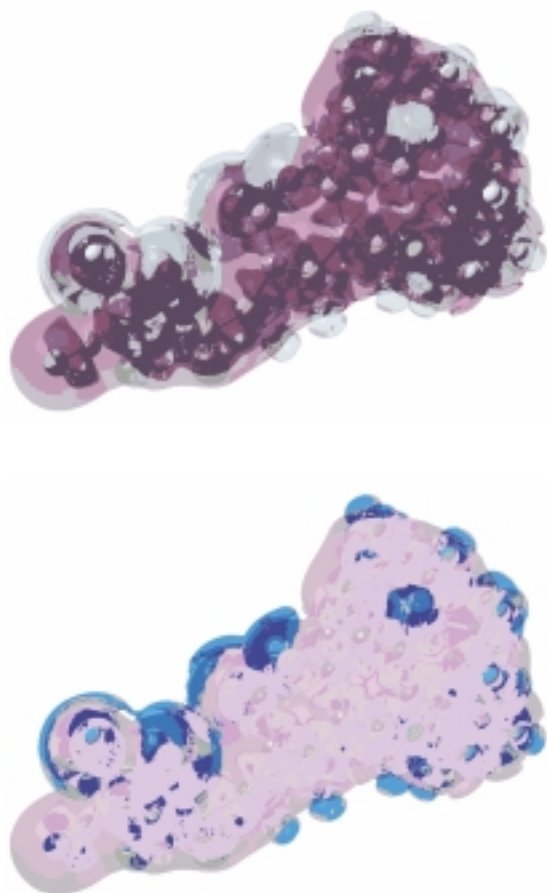

Figure 10: Calculated electron density difference between first excited singlet and ground state of coumarin derivative dye (top: negative values enhanced, below: positive values enhanced)

As regards the first excited state, the high degree of correlation indicated by the semi-empirical calculation (or by the difference between the 8eV MO difference and

the observed 1.8eV excitation) makes it difficult to succeed with a simple calculation. Linear combinations of excitation of single electrons between MO's (called CIS) fail to converge, and a time-dependent Hartree-Fock (TD) [19,20] solution contains spurious states, which however moves rapidly up in energy, as the ground state calculation includes more and more correlation (HF to B3LYP). The B3LYP +TD predicted energies are 0.70eV (triplet) and 1.3eV (singlet), followed by another singlet state at 1.44eV and another triplet at 1.58eV.

If the molecular orbitals are evaluated on the basis of the interacting wave functions, they become more correlated and have smaller LUMO-HOMO energies than those obtained from the HF ground state calculation. For example, the B3LYP LUMO-HOMO energy is 1.8eV (down from about 8eV in HF). On the other hand, the expansion of excited states on the more correlated MO basis has fewer components. This shows that the effect of truncating the configuration space is still felt. For example, the calculation of triplet excited states using a complete active space configuration method [21] does better when started with a basis or orbitals that are all spin=1.

Fig. 10 shows the electron density difference between the first singlet excited state of the coumarin-derivative, and the ground state, using the large basis HF+TD calculation. The excited state comprises 15 significant MO excitation pairs. The density difference shows the expected effect already surmised from the HF ground state MO's, that the excitation moves electron density from the coumarin core to the peripheral arm added to the molecule. It would then be natural to assume, that this is from where the transfer to the anatase surface, upon which the dye sits, takes place. This interpretation is supported by the large dipole moment found in the calculation (13.7 debyes).
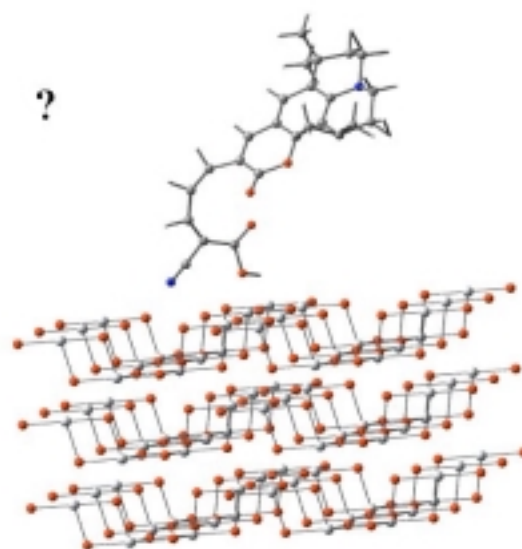

Figure 11: Possible attachment of coumarin-derivative dye to anatase surface.

The precise attachment of the dye to the anatase surface might be investigated by a combined optimisation of the dye plus a chunk of semiconductor, with the distance and rotation angles of the dye relative to the surface as parameters (cf. Fig. 11). A recent study of a similar material has revealed the nature of surface

distortion and surface Ti and O molecules [23]. The distortion only penetrates one layer down, in contrast to the over 10nm thick space charge regions in surfaces of solids.

4. CONCLUSIONS

The investigations of dye structure and electronic excitations have on one hand demonstrated, that there is today computer power enough to perform realistic quantum chemistry calculations for large molecules, although the most time-consuming models must be avoided (on a state of the art PC, optimisation may take a month of CPU, while single excited state calculations take days to weeks, depending on the complexity of the model selected). On the other hand, it is also seen that on the theoretical side, there are still a number of questions regarding the approximations used. This implies that many models would typically have to be tried, and that a good deal of experience is needed in order to evaluate the output from the models. A number of further "handles" on the calculations, not discussed here, is the comparison of measured spectra (IR, NMR, etc.) with those predicted by the calculations. In summary the quantum chemistry models offer tools for improving the understanding, but it is not clear that they take less time than enlightened trial and error approaches in the laboratory.

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