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PHOTOEMISSION STUDIES OF MIXED SENSITIZER MOLECULAR SYSTEMS

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Abstract The formation of mixed molecular layers is technologically important but the understanding of such molecular systems is limited. The comparative analysis of photoemission experimental results near threshold from organic dye layers, both in pure form and with a second kind of molecules present, shows that the energy levels of the dye molecules are affected by the presence of the foreign species. A theoretical model is presented for the calculation of the observed shift of the energy levels from Coulomb interactions in mixed aggregates and the results are applied to the study of the mechanism of supersensitization.

INTRODUCTION

For a system of dye molecules adsorbed on a crystal or on an amorphous substrate we have no single-valued energy levels, but a distribution of values which depends mainly on the density of charged surface defects.[1] A detailed study of the photoionization yield curve near threshold has shown that the experimental results can be verified by suitable macromolecular orbital calculations.[2] The calibration of this method of calculation allows us to compute molecular ionization energies[1,2] and electron affinities[3] with confidence. The interplay between theory and experiment has been particularly helpful for the study of the effect of aggregation and the substrate on the energy levels of these adsorbed molecular systems. It is clear now that the Coulomb effects are important and lead to considerable displacements of the energy levels,[4] which have been found to shift according to the mode of aggregation and the presence of nearby charged defects.[1-6,9]

The applications of these results are very interesting as they are connected with the mechanism of spectral sensitization of semiconductors,[5] the primary photographic process,[6] contact charging for the separation of minerals,[7,8] problems of energy conversion, etc. Well known experimental facts, which were not understood before, found convincing explanations by using only measurable quantities.[6,9] Furthermore since interest on the sensitization of ZnO, CdS, AgBr, and

other semiconductor electrodes continues, with a resulting wealth of new experimental data and fresh techniques,[10-15] it is essential to learn more about the intermolecular interactions for various forms of aggregates, as for example the J-aggregates and the H-aggregates.

The study of mixed molecular aggregates is more difficult, but is important for the understanding of the supersensitization of semiconductors by the combination of a dye and a supersensitizer molecule.[16,17]

EXPERIMENTAL SECTION AND RESULTS

The ionization energy of the dye molecules has been measured as an external photoelectric effect. The normalized photocurrent is plotted as a function of photon energy and rises exponentially up to a point, which determines the most probable value.[1]

The organic dye molecules used in this work are:
1,1'-diethyl-2,2'-cyanine halides (Pseudocyanine): PSC
1,1'-diethyl-2,2'-carbocyanine halides (Pinacyanole): PIN
3,3'-diethyl-thiacyanine halides (Thiacyanine): THC
3.3'-diethyl-thiacarbocyanine halides (Thiacarbocyanine): TCC
3,3'-diethyl-thiadicarbocyanine halides (Thiadicarbocyanine): TDC
3.3'-diethyl-thiatricarbocyanine halides (Thiatricarbocyanine): TTC

The electron affinity has been measured by the electron beam retardation method (EBR)[18] and has been corrected to correspond to the most probable value, Ea, of the molecular population.[3]

It is interesting that the analysis of the ionization energy distribution for a sample of molecules adsorbed as a monolayer on a substrate is exponential, rather than Gaussian, and its parameters are derived directly from the experimental data by a method which has been described in detail elsewhere.[1,2]

The results for the most probable values of the ionization energy, Ei,and the electron affinity, Ea, of the adsorbed molecules in monomolecular aggregates are given in Table I.

TABLE I Experimental results for the ionization energy, Ei, and the electron affinity, Ea, of molecules adsorbed on CdS

Molecule	Ei (eV)	Ea (eV)
PSC	5.95	2.3
PIN	5.35	2.4
THC	6.40	2.3
TCC	5.68	2.45
TDC	5.30	2.55
TTC	5.05	2.65

It should be emphasized that the Ei values are about 0.5 eV higher than the threshold values[2] and that the values of Ea are lower by about 0.7 eV than those of the EBR method.[3,18]

For the mixed molecular systems we have measured the photoemission current from PSC with an admixture of THC and we have compared it to that of pure PSC and THC.[16] We find considerable photocurrent enhancement around the photon energy of 5.3 eV, which is near the instrumental threshold for PSC while the threshold for THC is still higher. This shows in a direct way that the addition of THC lowers the ionization energy of a fraction of the PSC molecules by an estimated amount of about 0.6 eV.

CALCULATION OF THE ENERGY LEVELS OF MIXED AGGREGATES

Macromolecular calculations have already been developed,[2,3] which permit us to calculate the energy levels of conjugated ionic molecular aggregates. The calculation starts with one molecule, using Roothaan's SCF formulation for closed and open shell configurations. The external charges are included in the calculation by adding the coulomb repulsions to the matrix elements of the core, running over all π electrons of the molecule. The ionization energy is then calculated as the difference between the total binding energy of the ionized state and that of the ground state, taking into account the reminimization of the system of the remaining π electrons after ionization. A correction is then computed, which arises from the effect of the π electron removal on the sigma framework of the molecule (sigma deformation correction). Finally, there is a small correction for the effect of the induced dipole moments in the anion, on the receding electron.

The calculation for a linear aggregate of given geometry is performed considering one molecule of the aggregate. All the charges, on the atoms in the cores of the molecules in the aggregate and on the anions, are considered by their Coulomb interactions. This calculation gives new charges which are applied again for a new calculation and this is done as many times as it is required for self consistent results. This procedure is applied for an infinite linear aggregate. The first and last molecules in the chain need special attention. The position of the anions is determined also during the same cycles by minimizing the electrostatic interactions. We find that the aggregation effect on the ionization energy is a decrease of about 0.6 eV. The charged defects of the substrate are taken into account by a Monte Carlo calculation,[1] and are responsible for the spread of the values of Ei and Ea.

The calculation for the mixed aggregates is somewhat more involved. First, calculations for pure PSC and THC aggregates are performed. The resulting charge densities are then used for SCF-MO calculations for a THC molecule inside the PSC aggregate and for the PSC neighbouring molecules. The same procedure is repeated as many times as needed for

self consistent results, for the charge densities, up to the fourth decimal place. It is usually sufficient to perform three cycles, since the convergence of this method is very good. The results show that the introduction of a THC molecule in a PSC aggregate lowers the Ei of one of its neighbours and increases that of the other. This effect is about 0.6 to 0.7 eV depending on the assumed aggregate geometry. The second neighbour PSC molecule on the same side is also affected by a lowering of Ei, of about 0.2 eV, while for the third neighbour the lowering is negligible.

DISCUSSION

The results we have mentioned allow us to apply measurable energy levels to the mechanism of supersensitization of semiconductors by a sensitizer dye and a proper organic molecule, called supersensitizer. The older models of Gilman[19] and of Nelson[20] are energetically equivalent: Using the exitation energy, Ex, of the PSC, one electron is transferred to the PSC molecule from the supersensitizer (SS), ending with a supernumerary electron bound to the SS and an electron missing from the SS. This sets a limit on the ionization energy of the supersensitizer, Ei(SS): $Ei(SS) \leq Ex + Ea(PSC)$
otherwise the electron transfer cannot take place. Given the values of Ea(PSC) = 2.3 eV (Table I), and Ex = 2.2 eV, this limit is 4.5 eV. However, it is well known[21] that the THC and TCC molecules with ionization energies 6.40 and 5.68 eV, respectively (Table I) are supersensitizing PSC, while the TDC molecules, with Ei = 5.30 eV, are not. Even if we take the Ea(PSC) value of 3.0 eV from the EBR method without adjustment for the distribution the limit for Ei(SS) is 5.2 eV, clearly much lower than that of THC and TCC.

It is therefore, quite evident that the models of Gilman and Nelson cannot be supported by these data. A new model has been proposed by Nelson and Yianoulis,[16] which explains the supersensitization as a lowering of the ionization energy of a fraction of the sensitizer molecules, by the presence of the supersensitizer molecules in the aggregates.

The calculation model we have described here can be extended to other cases, as well, and can be improved for better accuracy. However, the main conclusion does not depend on the detailed results, but on the fact that the presence of the supersensitizer has a rather large effect on the ionization energy of some sensitizer molecules. The fraction of efficient sensitizers is then increased according to the distribution of ionization energies[6] which need revision in order to include the supersensitizer effect. Then one can easily find this fraction by integration.

We have assumed that electron transfer is the crucial act in dye-sensitization and that the J-aggregate acts as an antenna which

transfers the exitation energy to the sites where a supersensitizer molecule is present. In this model the efficiency of sensitization, which is energy-limited, is increased by the supersensitizer through the displacement of the energy levels of the sensitizer during the time of formation of the film on the substrate.

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