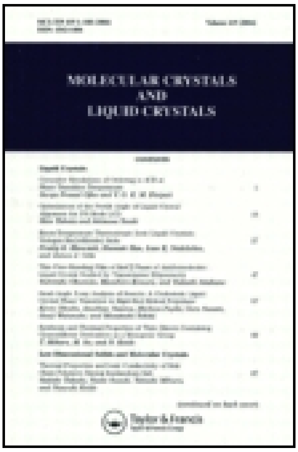

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Distribution of Ionization Energies of TCC and TDC Molecular Surfaces

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DISTRIBUTION OF IONIZATION ENERGIES OF TCC AND TDC MOLECULAR SURFACES.

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Abstract We have measured the ionization energy of multimolecular overlayers of dyes on glass. The experimental and theoretical results on the position of the energy levels of the sensitizer dye molecules used, thiacarbocyanine (TCC) and thiadicarbocyanine (TDC), show that the ionization energy of the surface molecules is displaced by their interaction with equivalent point charges in their neighborhood. Such charged sites exist not only on crystalline and amorphous substrates, but also on molecular crystal surfaces. We have extended our earlier calculations for adsorbed molecules of pinacyanole on polycrystalline substrates to molecular layers of TCC and TDC. The results are interpreted in terms of the density of charged defects, the geometry of the external molecular layer and the effective distance of the molecular "ionization center" from the surface.

INTRODUCTION

Photoionization experimental results for dye molecule monolayers, adsorbed on cadmium sulfide (CdS), pyrex glass and vycor glass, have been studied systematically and gave us new insight concerning the problem of the determination of ionization energies of adsorbed molecules[1,2,3]. The experimental investigation has shown that, within the experimental error, there was no temperature dependence of the exponential tails of the photoemission curves from dye molecules. It is of considerable interest to note that the slope of the semilog plot, corresponding to the yield of photoelectrons per incident photon as a function of photon energy, falls off with a slope of $(4kT)^{-1}$.

Therefore, one should understand the nature of these tails near threshold in order to be able to define the molecular ionization energies from the experimental data. This problem is not a simple one. It has been solved by the combination of experimental and theoretical results. The hypothesis that the randomly distributed charged defects on the substrate surface may cause a perturbation of the energy levels of adsorbed molecules, leading to a distribution of molecular ionization energies, has been tested extensively in pinacyanole. The same hypothesis has been applied to explain in a natural way, without the use of adjustable parameters, many phenomena of spectral sensitization. The results have always been satisfactory[4,5,6,7,8]. In addition, comparison of the electron affinity measurements by the electron beam retardation method with Monte Carlo simulations, has revealed that the electron affinity is also affected by charged defects in the vicinity of the molecules[9,10].

The purpose of this work is to examine the distribution of ionization energies of thick, multimolecular films, and to interpret the relationships between these experimental results and the corresponding for the monomolecular layers. The defect distribution in molecular crystals may also be inferred.

EXPERIMENTAL PROCEDURE

The dye film is applied on glass substrates, forming the photocathode, for an external photoelectric effect measurement. The photocathode is fashioned from a cylindrical glass piece with an appropriate cut at the end for exposure of the film to the incoming photons. The distance between the end of the photocathode and the first dynode of the electrostatic multiplier used is about 1 mm and the axis of the cylinder coincides with that of the multiplier. The dye is applied on the substrate, in a pure N_2 environment, from a solution containing 100, 200 and 300 mg/liter in absolute ethanol. It is known[1] that solutions of about 100 mg/liter give monolayer coverage. Therefore, we expect a multilayer film to be deposited on the substrate and this is confirmed by the experiment; we find that the ionization energies from the films formed using the dense concentration, are essentially the same as for the molecular solid dye.

The cathode is mounted into the vacuum chamber and is pumped down to 10^{-6} torr, with a preliminary vacuum system. Then, the pumping is continued using an ion pump, which is permanently mounted on the vacuum chamber. The pressure reaches 10^{-8} torr when the photoemission measurements are performed.

We have used the dye molecules: Thiacarbocyanine (TCC) with the structure 3,3'-diethyl-thiacarbocyanine chloride and Thiadicarbocyanine (TDC) with the structure 3,3'-diethyl-thiacarbocyanine chloride. These molecules were selected for possible observation of the effect of chain length on the final results. The photoionization has been measured for partial monolayer coverage and for monolayers in order to check the equipment, by comparison with older measurements for monolayer coverage[1].

RESULTS

The log of the normalized photoionization current per photon (in arbitrary units) as a function of photon energy is shown in Figure 1a, for a multilayer structure of TCC on a pyrex glass substrate. It has been prepared from a solution of 300 mg/lit of the dye in absolute ethanol. For comparison we present in Figure 1b the corresponding results for the monolayer (100 mg/lit). It is of interest that these results show only a small difference in the slope of the rectilinear part, being slightly larger for monolayers, and reduced photocurrent at the very low photon energy points. The photon energy, corresponding to the high energy end of the rectilinear part, (E_c), determines the "unperturbed"[1,2] ionization energy of the molecular population and is about 0.1 eV higher for the multilayer. Figures 2a and 2b show the corresponding experimental results for the TDC multilayer and monolayer coverage, respectively.

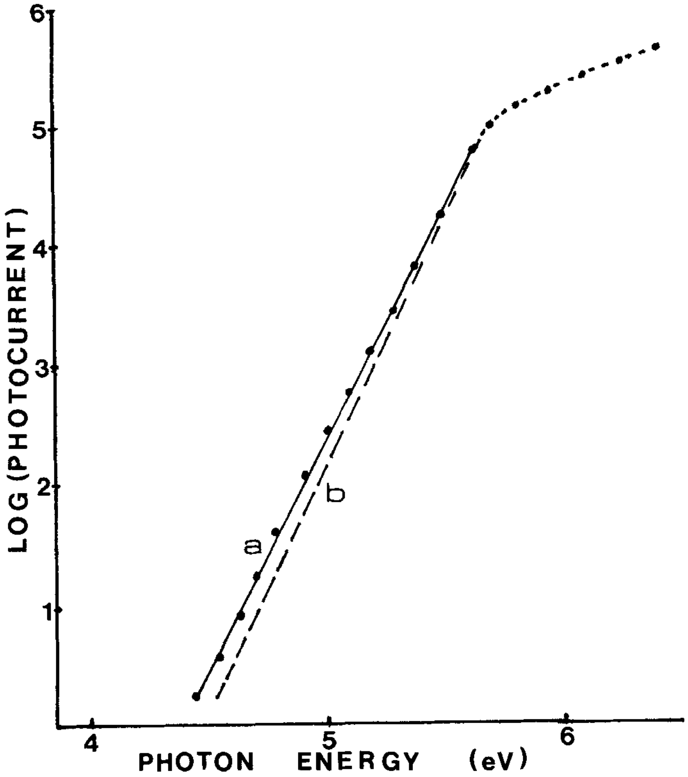

FIGURE 1 Logarithm of photoionization current per photon, as a function of photon energy. (a) for TCC multilayers and (b) monolayer, on pyrex glass.

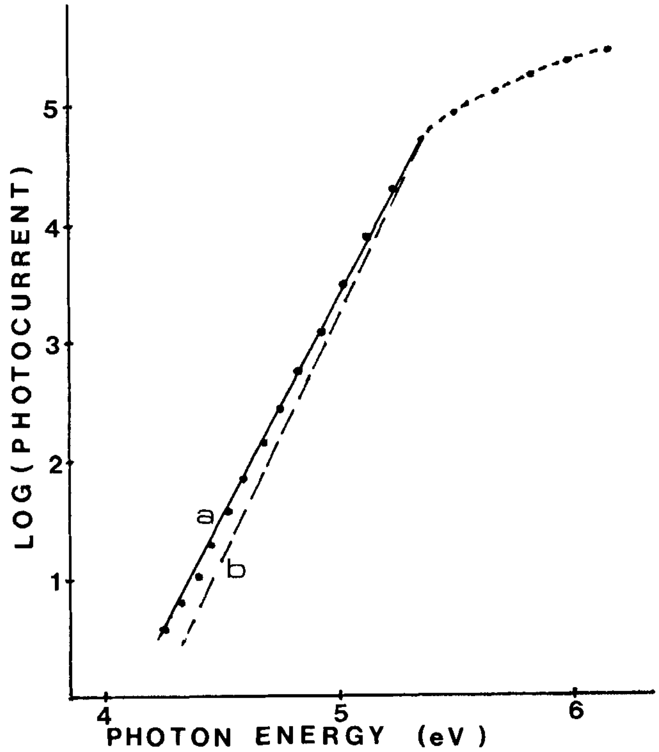

FIGURE 2 Logarithm of photoionization current per photon, as a function of photon energy. (a) for a TDC multilayer and (b) TDC monolayer, on pyrex glass.

In Table I we summarize the results of measurements for the two molecules and various concentrations of the dye solutions which have been used for the preparation of the overlayers.

TABLE I Slope of the rectilinear part of the photoionization curve, S(eV^{-1}) and "unperturbed ionization energy" E_c(eV) for TCC and TDC dye overlayers on glass. The lowest concentration corresponds to monolayer, the other two to multilayers.

Concentration	T C C		T D C	
(mg/liter)	S(eV^{-1})	E_c(eV)	S(eV^{-1})	E_c(eV)
100	3.9	5.7	4.0	5.4
200	3.8	5.8	3.9	5.5
300	3.8	5.8	3.8	5.5

DISCUSSION

The experimental results for multilayers show that the normalized photoemission curve near threshold, as a function of photon energy, is essentially the same with that for monolayers. Therefore we conclude, following our interpretation for the shape of these curves[1,2], that the distributions of molecular ionization energies for thick dye films and monolayers are comparable. The distribution of charged defects in the molecular phase is determined, in this indirect way, to be of the same order of magnitude as on the glass substrate. On the basis of these results, we believe that there may be a point for a more detailed examination of this problem, in terms of fine differences observed in various substrate - molecule combinations.

The slope of the photoionization curves for the multilayers is only slightly larger than that for the monolayer. This can be explained by the fact that the energy levels of the multilayer are perturbed by the combined charged defects, on the substrate and in the molecular overlayer.

The slightly higher value of E_c, by 0.1 eV, can be attributed to the longer distance of the molecules in the outermost layer from the substrate, which has a net negative charge, and causes a small uniform decrease of the ionization energy of adsorbed molecules. SCF-MO-LCAO calculations for molecular overlayers show that the polarizable environment of the molecule can cause a small additional shift of the E_c of the order of 0.2 eV. These calculations are combined with the ideal lattice effect and preferential adsorption results[3,11] in order to perform Monte Carlo simulations.

Evidently, there is a large number of parameters affecting the spread of the ionization energies of thick dye films: the geometry of the outmost molecular layers, the stacking mode, the effective distance of the molecular "ionization center"[1,3] from the surface, D_z, and the density of equivalent charge defects on the substrate, D_p (positive) and D_n (negative). The number of defects in the molecular phase is treated as an adjustable parameter. Unfortunately it is impossible to obtain all these quantities from photoionization experimental data by comparison with such simulations. Nevertheless, we can obtain resonable distributions of ionization energies, assuming plausible values for the parameters: D_z=7.5 Å, D_p=2.4x10^{11}/cm^2 and D_n=2.5x10^{11}/cm^2.

The main conclusion from a number of simulations, generating theoretical distributions of ionization energies, is that for the multimolecular films of TCC and TDC we obtain the experimental distributions of molecular energy levels, assuming reasonable values for the parameters. The distributions are similar to the corresponding for monomolecular films.

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