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ABSTRACT

Electron transfer from the excited state of tetra-iodo, tetrachloro fluorescein (rose bengal) to the conduction band of TiO_2 has been studied through photoelectrochemical techniques. The measured transfer rate was correlated with information from absorbance and adsorption measurements of this dye molecule on the (001) surface of the single crystals used as electrodes.

The quantum efficiency for the photo injection of electrons was determined to be 4.0×10^{-3} independent of the pH of the electrolyte and the dye surface concentration. With these data, an argument is given supporting the existance of excitation transfer among the dye molecules on the surface. A temperature study of the electron transfer yielded an activation enthalpy of 6.7 ± .5 kcals/mole with a pre-exponential factor of 4×10^3. A heat of adsorption of 7.6 ± .5 kcals/mole for this dye on TiO_2 single crystals was derived from analysis of adsorption isotherms measured at 21.5° C and 36.5° C.

In addition to the photooxidation process, a photoreduction was also observed upon cathodic polarization of the semiconductor. Action spectra revealed participation of solution dye molecules in this reaction; the reduction rate is dependent upon oxygen concentration in solution. It was concluded that the oxidized dye in solution accepts an electron from the TiO_2 to generate this current. This photoreduction was found with triphenylmethane and thiazine dyes as well as with other fluorescein derivatives.

INTRODUCTION

In the process of spectral sensitization excited dye molecules adsorbed on the surface of semiconductors transfer charge carriers to the underlying substrate[1]. If the semiconductor is used as an anode in an electrochemical cell, the charge transfer process can be monitored as electrical current[2]; thus, the ability of a dyestuff to sensitize can be simply and quantitatively measured. Use of this electrochemical cell technique has greatly facilitated investigations in spectral sensitization. Oxidation of the dye takes place through transfer of an electron from a molecule's excited energy level to the conduction band of the semiconductor. Anodic polarization is required for detection of this reaction. Although not the subject of this investigation, reduction of photoexcited dyes is also known to occur through a valence band mechanism which requires cathodic polarization. However, this can only be observed in compounds with a high hole mobility such as SiC or GaP[3,4].

It is apparent that the relative energies of a dye's molecular orbitals and the semiconductor bands are critical in determining that dye's ability to sensitize[5]. An oxidation reaction requires a matching of the conduction band and the dye's excited state energy while the reduction reaction depends upon the overlap of the valence band and the vacant molecular ground state. Efforts have been made in photographic research to confirm these correlations[6].

Another requirement for efficient charge transfer is the absence of quenching of the excited dye caused by energy transfer to the solid substrate. Overlap of the fluorescence spectrum of the dye and the excitation spectrum of the semiconductor must then be avoided. For efficient electron transfer, semiconductors with band gap energies greater than the excitation energy of the dye are required. When working with dyes which adsorb in the visible range, the choice of solids is limited to wide gap semiconductors with band gaps greater than 3 eV, such as ZnO, SiC, and TiO_2.

In most electrochemical inviestigations of spectral sensitization, water soluble dyes such as rhodamine or fluorescein derivatives have been employed as the sensitizating species[7-10]. The magnitude of the resultant oxidation current has been found to depend upon a number of experimental variables. Light intensity, electrolyte concentration, surface roughness, and solution pH all influence the rate of charge injection. The addition of reducing agents such as hydroquinone or allylthiourea greatly enhances the efficiency of sensitization through a photoreduction of the excited dye molecule[8]. Halides such as Cl^-, Br^-, and I^- can also serve as reducing agents[11,12].

Only those molecules adsorbed on the surface of the semiconductor participate in the sensitization process; yet, little direct information about the condition of the adsorbed dye has been established for the electrochemical investigations reported in the literature. For example, the amount of dye adsorbed on the surface, the degree of aggregate formation, and the heat of adsorption were not known. Inferences have been drawn concerning these points through determination of the photocurrent behavior as a function of the pertinent parameters such as solution concentration or light frequency[7-10].

In order to substantiate these conclusions we believe that it is necessary to correlate the photocurrent data with information from adsorption isotherms of the dye on the electrode surface. With isotherms at different temperatures it becomes possible to derive an activation enthalpy for the charge transfer process. A description of the photoelectrochemical behavior of a dye and substrate cannnot be complete without consideration of this information.

We have attempted to obtain such a complete description through selection and study of a system consisting of the xanthene dye rose bengal (tetra-iodo, tetra-chloro fluorescein) and TiO_2 (rutile). The large single crystal of TiO_2 that are commercially available make it possible to establish an adsorption isotherm for rose bengal through an elution technique[13]; absorbance spectra of the adsorbed dye can also be obtained. Since the crystal is inert to electrochemical dissolution, this adsorption and absorbance information will still be applicable when these same crystals are employed as semiconductor electrodes in the measurement of the photoelectrochemical oxidation of rose bengal.

EXPERIMENTAL

Rose bengal was obtained commercially and purified through recrystallization in ethanol. An extinction coefficient of 1.04×10^5 at the absorption maximum in methanol was used for this dye as reported in the literature[14]. In these experiments all dye solutions were made with distilled water and were 1 M in KCl. In this solution the dye accepted an electron form a mercury electrode at a potential of −1.08 V vs. a saturated calomel electrode (SCE).

The TiO_2 was purchased from Nakazumi Crustals of Osaka, Japan. The crystal came as a long boule grown along the "c" axis by flame fusion. Slices 250 μ thick with a cross section of about 1.5 cm^2 were cut with a string saw so that the (001) basal plane was exposed.

The crystals were polished to a 1 μ finish and then heated in a vacuum oven for four hours at 650° and 5×10^{-6} torr to increase their conductivity. This treatment creates oxygen vacancies which serve as donors[15].

Prior to use they were etched for one hour in conc. H_2SO_4. The final surface was galssy smooth with some ripples that were barely visible to the eye.

The concentration of donors in the crystal was established through capacitance measurements[16] to be 5×10^{18}/cc. The flat-band potential of these crystals exhibited a frequency dependence over the range of 1 to 10 kHz becoming more negative with increasing frequency. The slope of the resultant Mott-Schottky plots, however, remained constant. A General Radio 1650A impedance bridge was used in conjunction with a Hewlett Packard 3310A function generator.

Ohmic contacts to the crystals were made through vacuum deposition of indium. A window of several mm^2 was masked during deposition to allow illumination of the semiconductor surface through the electrode.

Adsorption isotherms for the adsorption of rose bengal on these TiO_2 single crystals at 21.5° C and 36.5° C were determined using an elution technique[13]. The crystals were immersed in dye solution of up to 4.38×10^{-4} M (all of which were 1 M in KCl). The equilibrium time varied with temperature and dye concentration but was always less than 20 minutes. After a 20 minute immersion the crystals were removed from the dye solution and washed with decane in which rose bengal is insoluble.

Absorption spectra of the dye adsorbed onto the surface of the electrode are required for determination of both quantum efficiency of charge injection and adsorption isotherms. However, even with such a large extinction coefficient, the maximum absorbance of a monolayer of the dye is ca .01. In order to increase the measurement precision. a stack of three crystals, with six surfaces, was aligned in the beam of a Cary 118 spectrophotometer for absorbance measurements of dye adsorbed on these surfaces. Another stack of three crystals was placed in the reference beam of the spectrophotometer to compensate for the absorbance of the crystals.

The dye adsorbed on these crystals was eluted with methanol and saved. The product of the concentration of the dye in the eluent and its volume yielded a figure for the absolute amount of dye adsorbed on the crystals. Normalized to unit surface area, this figure can be correlated with the integrated absorption of the adsorbed dye. From it, points on an adsorption isotherm can also be obtained.

The electrochemical cell was constructed so that the light passed through the TiO_2 electrode to the active surface before being absorbed in the bulk of the solution. A Pt counter electrode and a saturated calomel electrode used as a reference were separated from the main body of the dye solution by glass frits. Provisions were made for addition of reagents and stirring of the electrolyte with gas. The electrolyte solutions were not deoxygenated in view of the oxygen evolution at the TiO_2 surface at anodic bias potentials. A thermal jacket surrounded the cell for temperature control. The cell was shielded by a Faraday cage of copper mesh.

Photocurrent measurements were made with the experimental set-up depicted in Fig. 1. A 450 W Xe high pressure lamp served as a light source; a Bausch and Lomb high intensity monochromator or interference filters were used for wavelength selection. The light was modulated by a mechanical chopper at frequencies ranging from 3 to 11 Hz. Between photocurrent measurements the TiO_2 electrode was washed in successive baths of acetone and distilled water.

Potentiostatic control of the electrode was maintained with a Wenking fast rise (1μ sec) potentiostat; potential ramps for voltage sweeps were supplied by a PAR 175 Universal Programmer. The photocurrent was amplified by a PAR 181 current sensitive amplifer and them demodulated with an HR-8 lock-in amplifier.

Light intensity was measured with the use of silicon solar cell and a Hewlett-Packard 8330A Radiant Flux Meter with an 8334A radiant Flux Detector. In the experiment requiring signal averaging, a Nicolet NIC-80 computer was used.

RESULTS

Adsorption Measurements

Adsorption isotherms for rose bengal on the TiO_2 crystals were obtained at two temperatures 21.5^0 C and 36.5^0 C as shown in Fig. 2. Langmuir type behavior was observed with plateaus attained at solution concentrations of about 1 x 10^{-4} M. A relation[17] describing Langmuir behavior for dyes on crystal surfaces may be written:

$$\frac{C}{C_s} = \frac{C}{C_m} + \frac{1}{C_m K} \quad (1)$$

where C is the solution concentration of the dye (mmoles/ml)

C_s is the surface concentration of the dye (mmoles/cm^2)

C_m is the surface concentration of the dye at monolayer coverage (mmoles/cm^2)

K is an adsorption constant (cm^3/mmole)

Plotting the data of Fig. 2 according to Eq. (1) should yield a line with a slope equal to the inverse of the monolayer concentration. The information derived from such an analysis is assembled in Table 1. Assuming a surface with a roughness factor of unity, the area for each molecule can be calculated to be 75Å^2 at 21.5° C and 81Å^2 at 36° C.

Absorbance spectra of the dye adsorbed on the crystal indicate adsorption in predominantly the monomer form. The spectra of Fig. 3 revealed a gradual increase in surface dimer concentration which is reflected in a greater relative adsorption in the high energy shoulder. Solution spectra of the dye are shown in Fig. 4 for comparison.

Dye Photooxidation

These TiO_2 crystals used in the adsorption measurements were fashioned into electrodes for use in the electrochemical set-up. Immersed in an electrolyte containing the dye, the crystals were illuminated with light in the spectral region of the dye; at anodic potentials an oxidative photocurrent was observed. With this bias sufficient to draw off all injected charge, the photocurrent at the absorbance maximum was recorded as a function of time (Fig. 5). A fast decay was observed which was followed by a slower long term decline in the photocurrent. The decay can be attributed to an accumulation of the oxidized dye on the surface of the electrode with the oxidized form apparently stable enough to permit regeneration of the dye (*vide infra*).

A coulometric analysis of the current passed through the electrode in the first 500 sec of illumination revealed that only 8% of the dye on the surface of the electrode has been oxidized. With the electrolyte at pH 6.6 and 21.5° C, the quantum efficiency for the initial charge injection was determined to be 4.0×10^{-3}. Here the quantum efficiency is defined as the number of electrons transferred per photon absorbed by the dye.

After a quasi-steady state was reached in the time decay of the current corresponding to point A of Fig. 5, the light was swept through the spectral region of the dye, giving the spectrum of Fig. 6b. This curve compares very well with the absorbance spectra of Fig. 3.

Recent investigations[11,12] into the sensitization of ZnO by rhodamine B have shown that Cl^- can be photooxidized by the adsorbed dye in an excited state. It is necessary to show for the system rose bengal/1 M KCl/TiO_2 that chloride does not photoreduce the excited dye since the electrochemical properties of the reduced dye are not of interest in this work.

This was accomplished through the measurement of the quantum efficiency of electron injection as a function of chloride concentration when the electrolyte is 3.2×10^{-5} M in the rose bengal (Fig. 7). To evaluate the quantum efficiency it was necessary to measure the optical density of the adsorbed dye at each concentration of KCl and correlate it with the observed photocurrent. The absorbance measurements were taken as described in the experimental section. Photooxidization of rose bengal at TiO_2 appears to be insensitive to chloride and the observed photocurrent may be seen to reflect the oxidation of the excited dye at the electrode surface.

With the use of a 560 nm interference filter, the photocurrent was measured as a function of the solution concentration of the dye (Fig. 8). Since the absorbance of the adsorbed dye for specific surface concentrations is known, a determination of the quantum efficiency as a function of surface coverage is possible. In Fig. 9 it can be seen that the efficiency of charge transfer is independent of surface concentration of the dye over the range investigated.

The dye molecule is adsorbed on the surface of the TiO_2 in the Helmholtz region of the double layer. Except when the semiconductor becomes degenerate, there is a negligible change of the potential drop across the Helmholtz layer with a change in the polarization of the electrode. However, through capacitance measurements this drop has been found to be dependent upon the pH of the electrolyte solution; for TiO_2 it has been reported to change by about 60 mV/pH unit[18]. This figure was confirmed for the crystals used in these experiments.

In order to find the extent to which a change in the Helmholtz potential drop affects the electron transfer reaction, the photocurrent was measured as a function of pH. This experiment has been done with rhodamine on ZnO[19] and is conceptually similar to current-voltage curves for reactions at metal electrodes. Measurements were taken from pH 5 to 11; acidic pH's were avoided because of protonation of the dye. A logarithmic plot of the photocurrent is seen in Fig. 9 as a linear function of pH with an average slope of $.07 \pm .01$.

The absorbance of the adsorbed dye layer was also measured as a function of pH and was found to describe a similar logarithmic relation with slope $.07 \pm .01$. The quantum efficiency of electron transfer must then be independent of the change in the potential drop across the Helmholtz region over the range covered by these pH experiments. The spectral characteristics of the dye were also examined as a function of pH. Absorption and fluorescence spectra exhibited no significant change over the pH range of interest indicating no pH dependent properties of the ground or excited state of the dye.

Temperature Dependence

Activation energy determinations in spectral sensitization have been confined to systems where the dye was adsorbed at a gas-solid interface or was applied to the solid as a thin film. In electrochemical systems some difficulties are encountered in the experimental determination of an activation energy. The potential of the reference electrode is a temperature dependent quantity, a condition which can hinder comparison of current densities at different temperatures. At sensitized electrodes, the use of water soluble dyes brings in another temperature dependent variable in the form of an adsorption isotherm.

As described earlier, adsorption information for rose bengal on TiO_2 at two temperatures was determined. It is important, too, to reiterate that the quantum efficiency of charge injection is not sensitive to the change in surface concentration that occurs between these two temperatures. Also, a change in the reference potential is unimportant because the semiconductor electrode can be polarized in a saturation region where a change in bias does not affect the photocurrent. An additional complication in a termperature study would be a temperature dependent potential drop across the Helmholtz layer at the electrode surface. Through capacitance measurements, this change in the Helmholtz potential drop at TiO_2 was measured to be $\pm$ 0.10 V over the 15^0 range between 21.5^0 C and 36.5^0 C. Through the pH study above, however, the effect of such a change in the Helmholtz region on the quantum efficiency is known to be negligible. With these variables determined, it should be possible to obtain an activation enthalpy for the photo-oxidation of rose bengal at a TiO_2 electrode.

In order to derive this quantity from photocurrent measurements, it is necessary to compute the temperature dependent quantum efficiency, $\Phi(T)$:

$$\Phi(T) = I(T)/(n \cdot A(T))$$

where T is the temperature; I(T) is the current density at T in electrons $cm^{-2}sec^{-1}$; A(T) is the absorption of the dye adsorbed on the electrode; n is the photon flux in photons $cm^{-2}sec^{-1}$.

Values for A(T) were taken from the absorbance spectra used to construct the isotherms of Fig. 2. Interpolation between the absorbances of 21.5° C and 36.5° C yields figures for A(T) at intermediate temperatures. I(T) was taken as the initial magnitude of the photocurrent before the time decay set in. A plot of the logarithm of $\Phi(T)$ vs inverse temperature should yield an activation enthalpy for the electron transfer.

The temperature dependence of the photocurrent between 21.5° C and 37.5° C was measured. $\Phi(T)$ was computed for each experimental point and used to construct the Arrhenius plot of Fig. 11. A slope of $6.7 \pm .5$ kcals/mole was obtained with a least mean squares fit. The pre-exponential factor was 4×10^3 within a factor of two.

These measurements began at room temperature; the solution was then heated to 37° C and data were taken as the solution cooled. Between measurements the TiO_2 electrode was washed in successive baths of acetone and distilled water. A twenty minute equilibration period in the dye solution was allowed prior to illumination; the acquisition of the data in Fig. 11 required several experimental runs.

Sensitized Photoreduction

The commonly observed bias dependence of the photocurrent from a dye-semiconductor pair can be seen in Fig. 12 for rhodamine B adsorbed on ZnO. The current rises from zero at cathodic potentials to saturation at a more anodic bias. Since KCl was used as the electrolyte in this system, it is the reduced rhodamine B that injects the electron to produce the current depicted in this figure.

In the system of rose bengal and TiO_2, however, the bias dependence of the photocurrent is characterized by the unusual features depicted in Fig. 13. Instead of the photocurrent disappearing at lower potentials, a reduction current set in which peaked at about -0.85 V.

The magnitude of this reduction reaction at -0.85 V was found to be linearly dependent upon the absorbance of the dye in solution. An action spectrum at this peak corresponds to the absorbance of the dye in solution depicted in Fig. 3. Stirring of the electrolyte increased the reduction photocurrent while deoxygenating the solution with N_2 greatly diminished it. Introduction of hydroquinone also resulted in a decrease of the reduction current. Stirring of the solution with air increased the current, but a subsequent changeover of stirring gases to pure O_2 did not result in any further increase. Thus, the concentration of excited dye in solution appears to be the rate limiting species. This reduction reaction could never be eliminated, presumably because of the dark current evolution of O_2 at the TiO_2 surface.

At a bias potential of -0.48 V where the photooxidation is still saturated (Fig. 13a), the photocurrent was found not to decay with time (Fig. 5b). The absence of a time decay implies that the dye on the surface oxidized by photoinjection of the electron is being regenerated during the course of the light modulation cycle. To substantiate this implication, the photocurrent response of the system was determined for one cycle of the chopping frequency at a bias of -0.49 V; in this manner the time scales of the oxidation and reduction reactions could be compared. This experiment was carried out with 3.6 Hz modulation using a signal averager.

The result shown in Fig. 14a is characterized by a very fast oxidative component which is gradually overcome by a slow rising reduction current. At this bias, evidently, a reduction reaction continually regenerates the rose bengal oxidized at the surface during the light portion of the chopping cycle. If the modulation period is lengthened in this signal averaging experiment, the rise time of the reduction current becomes evident (Fig. 14b). About 1-2 seconds are required for this reduction current to approach its diffusion limited maximum.

If the photocurrent at a positive bias potential is allowed to decay as in Fig. 5a, a cathodic polarization sweep will return the photocurrent to its maximum as seen in Fig. 13b. Thus, a monolayer of the dye can be regenerated from a surface covered with its oxidized form.

This photoreduction reaction was also observed with rhodamine B, eosin, crystal violet, malachite green, methylene blue and thiazine at the TiO_2 electrode. The regeneration of photooxidized dyes was observed for all dyestuffs which sensitized TiO_2 (as in Fig. 13b for rose bengal).

At a bias potential more negative than -0.24 V the net current flowing acorss the TiO_2 surface reflects contributions from several reactions, the dye sensitized oxidation and reduction, reduction of oxygen, and hydrogen and oxygen evolution from the conduction and valence bands of the semiconductor. These partial currents are depicted in Fig. 15.

The dark current at the electrode (Fig. 15a) reflects the evolution and reduction of oxygen at the surface and at more negative potentials, evolution of hydrogen. The potential dependence of oxygen evolution at the electrode (Fig. 15b) can be seen in the current-voltage characteristics of the TiO_2 intrinsic photocurrent. The photomodulated sensitized oxidation and reduction currents are superimposed upon these two background reactions. The influence of the dark reactions on the sensitized photocurrent is clear.

DISCUSSION

Adsorption Isotherm

From the absorbance spectra of the dye adsorbed on the TiO_2 crystals it is evident that the dye is adsorbed from solution in the monomer form. The spectra in Fig. 3 reflect a progressively larger fraction of surface coverage with a relatively small increase of 20% in the high energy shoulder where dimer absorbance occurs. This increase in surface dimerization can probably be attributed to the increasing concentration of the dimer in solution.

An estimate of the heat of adsorption of the dye may be made with data obtained from analysis of the adsorption isotherms. Gunther and Moisar[17] have adapted a Boltzmann expression to the Langmuir relation of Eq. (1) to obtain an expression for the heat of adsorption:

$$\Delta H = 2.3\ RT \log (D/C_m K) \qquad (2)$$

where $1/C_mK$ is given in Table 1 and D is the thickness of the dye layer when attached to the crystal surface. Using a 10 Å as an estimate for D, a ΔH of approximately 7.6 kcal/mole is obtained for both temperatures (see Table 1). Previous investigations[6] have determined that a heat of adsorption of this magnitude is indicative of weak Van der Waals interactions between the dye and the semiconductor. However, a ΔH of this size is considered large enough to insure mololayer coverage of the surface[17].

Implicit in the use of a Langmuir analysis of an adsorption isotherm is the assumption that ΔH is independent of surface coverage. This is probably true for the surface concentrations covered by these experiments. However, the data only extended down to a coverage of $\theta = 0.4$ so that use of this Langmuir analysis places no a priori assumptions on variations in ΔH below this limit. Indeed, it has long been established[20] that the heat of adsorption is greatest for the first additions of dye to the surface. Physically, this higher ΔH can be seen as the manifestation of a small number of more active adsorption sites which are preferentially occupied at low surface coverage. ΔH subsequently decreases as θ becomes larger with the differential heat of adsorption eventually tending to zero. It is not unreasonable to expect a similar θ dependence of ΔH for the adsorption of rose bengal on TiO_2 at small θ.

A complete coverage of the surface appears probable upon examination of the experimentally determined surface area/unit dye molecule. At 21.5° C with an assumed surface roughness factor of unity, each molecule occupies 75 $Å^2$ of the surface. Using models, a maximum of 100 $Å^2$ is expected for this dye. This would imply tight packing of the dye and, indeed, some increase in dimerization is present in the absorbance spectra. However, some degree of roughness greater than unity can be expected and the existence of a plateau in the isotherm suggests a not unreasonable minimum value of 1.3 for this etched surface.

Excitation of the rose bengal at the TiO_2 surface results in generation of an oxidative photocurrent with action spectra (Fig. 6) closely matching the absorbance of the adsorbed dye (Fig. 3a). The distinct difference between these spectra and the solution spectra of the dye excludes the probability of participation of solution species in the photooxidation reaction.

This comparison also shows that the surface spectra maxima are shifted about 15 nm to the red from the corresponding solution peaks. This effect is equivalent to that observed when the molecule is immersed in a medium of higher dielectric. In solution this red shift may be seem as a function of the index of refraction of the solvent. For the dye in methanol with an index of refraction, n_d, of 1.3288, the energy of the absorbance maximum, E_{ν_m}, is 18000 cm^{-1}; in acetone with n_d= 1.3588, E_{ν_m}= 17900 cm^{-1}; in pyridine with n_d= 1.5095, E_{ν_m}= 17600 cm^{-1}.

If the adsorption of the dye is due entirely to dispersion forces which are responsible[21] for the solvent shifts quoted here, an E_{ν_m} of 17800 cm^{-1} found for the action spectrum of Fig. 6 would correspond to $n_d \cong 1.4$ at the semiconductor surface. This would imply that the optical dielectric of the adsorbed layer is larger than that for the solution bulk. Studies[21,22] of this red shift have been made, but it has not yet been fully explained.

Excitation Transfer

The time decay of the photocurrent reveals that after a 500 second exposure to 560 nm light only 8% of the dye on the surface has been oxidized. Evidently, very few of the excited, adsorbed molecules are able to inject an electron into the cystal while in an excited state.

It is probable that the adsorption site of the dye plays a critical role in determining its ability to sensitize the substrate. Given a dye at the electrode surface, its adsorption orientation and its distance from the surface should vary according to the molecular details of its adsorption site. These details, for example, will be closely tied to the dye molecule's heat of adsorption. Those molecules with a high heat of adsorption will be more tightly bound to their sites and will be closer to the surface than those with lower adsorption heats. Less favorable sites bind the dye molecule more loosely and thereby would have less of an influence upon the adsorption orientation of the molecule. Consequently, dye molecules at different sites on the surface may be expected to exhibit different efficiencies of electron transfer.

In Fig. 5 a rapid decline of the photocurrent is seen which is followed by a slower, long term decay. Thus, those molecules on "reactive" sites which permit high quantum efficiencies of electron transfer can be seen to be quickly oxidized with the subsequent photocurrent due mainly to dye on "reactive" sites with lower quantum efficiencies. The remainder of the adsorbed dye must then be adsorbed at nonreactive locations.

As the surface concentration of the dye is increased it is not unreasonable to expect dye-dye interactions such as energy transfer to affect the efficiency of the charge transfer process. This point has been discussed in previous investigations[9]. These interactions could take place via a strong excitonic coupling as occurs in dimers or a weaker long range energy transfer. However, the absorbance spectra of Fig. 3 exclude all but the weakest of energy transfer interactions.

The data of Fig. 9 demonstrate that the quantum efficiency of charge injection remains constant over a range of surface coverage from 1.0 to 2.2 x 10^{-7} mmole/cm^2. This suggests two possibilities. Either the incidence of excitation transfer is negligible or its effect on the electron transfer efficiency has saturated before the coverage of 1.0 x 10^{-7} mmoles/cm^2 has been reached.

For any long range energy transfer between two dye molecules to be efficient, their separation should be no greater than about 50Å and their orientations should be compatible. At the lower limit of the surface coverage investigated, the dye is distributed over the surface with an average intermolecular distance of about 13 Å. If energy transfer occurs in this surface array, it would definitely drop off once the intermolecular separation passed 50 Å. This corresponds to a surface concentration of about 2 x 10^{-9} mmoles/cm^2 or θ = .01. It is evident that surface concentrations covered in this work are not low enough to decide between these two possibilities.

Further examination of the data in Fig. 9, however, provides a basis for postulating the existence of excitation transfer among the dye molecules on the semiconductor surface. It must be assumed, though, that the efficiency of electron transfer from the dye to the semiconductor is dependent on its site of adsorption and thereby on its energy of adsorption.

It has been discussed previously how a measure of this energy, i.e., the heat of adsorption, can be expected to decrease with increasing coverage of the surface with the last molecules adsorbed having the smallest heat of adsorption. Yet, the data of Fig. 9 show that the quantum efficiency of charge injection remains constant as an increasing number of the most weakly bound molecules are removed.

This experimental result is compatible with the above assumption only if the probability of excitation of a molecule at a reactive site is directly proportional to the number of quanta absorbed by the dye layer on the electrode surface. This implies transfer of excitation from non-reactive molecules to reactive molecules even at $\theta = 0.4$ where the intermolecular separation is 13 Å.

The greater part of the dye on the surface must then function as an antenna which absorbs the quanta of light and transfers the excitation to reactive sites where oxidation can occur.

Dye-Semiconductor Energetics

There are two main components in theoretical expressions[23] for the activation energy of an electron transfer reaction. One deals with the energy required to rearrange, or polarize, the environment about the electron so that transfer may occur. The other accounts for the work necessary to bring the reactants together within the required distance and in proper orientation to allow the electronic interaction necessary for transfer.

For the case of dye sensitized semiconductors, a relation describing the first of these contributions to the activation energy has been suggested by Gerischer[5]:

$$j \propto \exp\left(\frac{-(E_C-E_D-E^*)^2}{4\pi\lambda^* kT}\right) \qquad (3)$$

to affect the efficiency of the charge transfer process. This point has been discussed in previous investigations[9]. These interactions could take place via a strong excitonic coupling as occurs in dimers or a weaker long range energy transfer. However, the absorbance spectra of Fig. 3 exclude all but the weakest of energy transfer interactions.

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For the case of dye sensitized semiconductors, a relation describing the first of these contributions to the activation energy has been suggested by Gerischer[5]:

$$j \propto \exp\left(\frac{-(E_C - E_D - E^*)^2}{4\pi\lambda^* kT}\right) \qquad (3)$$

where E_c is the energy of the semiconductor conduction band; E_D is the energy level of the ground state of the adsorbed dye; E^* is the excitation energy; λ^* is the energy required to rearrange the atoms of the solvent molecules surrounding the excited dye so that they occupy positions compatible with the product species at equilibrium. These terms are pictorally defined in Fig. 16. The activation energy defined by Eq. (3) is $\Delta E^2/4_*$ where $\Delta E = (E_C - E_D - E^*)$ is the energy difference between the conduction band and the maximum of the excited singlet state of the dye on the surface.

As Fig. 16 shows, the molecular orbital energies of the dye are distributed about energy maxima owing to thermal fluctuations in the interactions of the molecule with the solvent. This time dependent variation in the positions of the atoms in the species which form the environment about the molecule of interest induces corresponding time dependent changes in the energy of its molecular orbitals. The range of this variation in the energy of the molecular orbital can be described by a distribution function[5]:

$$W(E) = \frac{1}{4\pi\lambda^* kT} \exp^{\frac{-(-E-E_D)^2}{4\pi\lambda^* kT}} \qquad (4)$$

The overlap of this energy distribution for the excited state with the density of states of the semiconductor conduction band will determine, according to Eq. (3), the rate of electron transfer from the excited dye to the semiconductor. If E_{D*} rests below E_C in Fig. 16, this overlap will be small and there will be a minimum rearrangement energy, ΔE, required of the environment about the dye for activation of the occupied electronic orbital to E_C from its mean value E_{D*}. In the case where E_{D*} is above E_C there will be no minimum polarization energy necessary for electron transfer and no contribution to the activation energy from this source.

The relative values of E_C for TiO_2 and E_{D*} for the dye in solution can be obtained easily. This is done through comparison of the reduction potential of the dye, $E_R = -1.08$ V, and the flat band potential of the semiconductor which indirectly yields the energy of the conduction band, $E_C = -0.5$ V (taken from literature sources[24,25] because a frequency independent flatband potential could not be obtained from capacitance measurements of these crystals). As seen in Fig. 16, E_C rests below E_{D*} for the solution dye species.

For the adsorbed dye, the energy difference between E_C and E_{D*} will not be equivalent to that for the solution species, as is depicted in Fig. 16 in the extreme limit where $E_{D*} > E_C$. This difference between adsorbed and solution species will depend on the potential drop across the Helmholtz layer at the surface and the position of the dye within this layer.

A change in the potential drop across the Helmholtz layer through variation of the pH of the electrolyte will thereby change ΔE for the surface dye. Varying ΔE changes the free energy of the reaction; the magnitude of this ΔG change will depend on the fractional distance, α, relative to the Helmholtz layer thickness, from the electrode surface to the plane of the chromophore. According to Eq. (3), if $E_{D*} > E_C$, a change in ΔE results in an exponential change in the electron transfer rate[26].

In contrast to this situation, the quantum efficiency of oxidation of excited rose bengal remains constant over the pH range from 5 to 12. This pH difference corresponds to a change in ΔE of $0.42 \cdot \alpha$ V revealing that the rate of the photooxidation is independent of the free energy of the reaction over this region of small change in ΔG. This indicates that E_D does not rest below E_C for the dye adsorbed on the surface of the semiconductor. Thus, there appears to be no minimum rearrangement energy required of the solvent for this electron transfer to take place, and the relation of Eq. (3) does not determine the rate of this electron transfer action. It is evident that the measured activation enthalpy of 6.7 kcal/mole for this electron transfer must originate in phenomena other than the polarization of the environment involved in the rearrangement process.

The most probable source of the activation barrier can be found in the second source mentioned above: the work required for the approach and orientation of the excited dye. Attribution of the activation energy to work terms requires some exploration since the reactive species is already adsorbed on the surface of the electrode. The contribution of the free energy of adsorption to the work has already been accounted for in the use of the quantum efficiency of the reaction in the activation analysis. This implies that adsorption does not guarantee the orientation and approach distance that may be required for reaction.

Electron transfer from the excited dye will originate at the regions of the chromophore where the electron density of the excited electron is localized. In order for these parts of the molecule to approach the crystal lattice to within the critical distance, additional repulsion from the crystal lattice may have to be overcome. The movement of the excited species into an energetically unfavorable adsorption orientation could also be necessary. If there is an intervening solvation sheath on the surface, this too, may have to be displaced before transfer can occur. Thus, it can be seen how work terms may be necessary for activation of an adsorbed species.

It has been implicit in the discussion thus far that only the singlet state of the dye is responsible for sensitization. With the proper energetic relationship to the semiconductor, the triplet energy level of the dye should be able, in principle, to contribute to the charge injection. If the sensitization were due entirely to electrons from the triplet dye, then ΔE would represent the energy difference between the conduction band and the dye triplet energy level.

In search of the role of the triplet in sensitization, the paramagnetic ions Mn^{+2} were added to the electrolyte to serve as triplet quenchers. No change in the photocurrent was observed. It has been suggested by Tributsch[27] that the lifetime of the triplet state of the adsorbed dye may already be shortened to the extent that it is relatively unaffected by the paramagnetic ions. In general, little evidence has surfaced in the literature[12] which has established the participation of the triplet state in this reaction.

Solution Photochemistry

The photomodulated reduction observed at the cathodically polarized TiO_2 was initiated by a solution species that is created by the interaction of excited rose bengal with oxygen. The role of oxygen in this reaction was demonstrated through the decrease in the cathodic current following deoxygenation by introduction of either N_2 or hydroquinone.

Investigation of the solution photochemistry of the senisitzing dyes used in this investigation has determined that their reactivity to oxygen is due almost exclusively to the activity of the triplet state[14]. The reduction photocurrent would also be diminished through addition of hydroquinone because of its ability[17] to reduce the triplet dye.

As triplets in solution, these dyes can either create singlet oxygen through energy transfer or they can be oxidized by oxygen:

$$^3D + O_2 \longrightarrow D + {}^1O_2$$

$$^3D + O_2 \longrightarrow D^+ + O_2^-$$

Both of these reactions result in products which could function as oxidants at the electrode surface:

$$^1O_2 + e^- \longrightarrow O_2^-$$

$$D^+ + e^- \longrightarrow D \qquad (5)$$

With the exception of triphenylmethane[28] compounds, the dyes which sensitize the reduction at the TiO_2 electrodes are known to produce singlet oxygen which can be reduced electrochemically at the TiO_2 surface. Although the lifetime of singlet oxygen in aqueous solutions is on the order of microseconds[29,14], it will be created as long as the triplet dye exists in solution. The lifetimes of the triplet states of these dyes, however, are in the millisecond range. In the dark segment of Fig. 14b, the sensitized photoreduction requires several seconds to decay, yielding a lifetime for the reactive species of about one second. Thus, while reduction of singlet oxygen is possible it cannot account for the long lifetime of the solution species reduced at TiO_2.

On the other hand, reduction of the oxidized dye in solution, Eq. (5), has been reported[28] at metal electrodes biased at potentials from 0.0 V to -0.5 V, an energy range in which the conduction band of TiO_2 rests. The feasibility of such a reaction occurring at TiO_2 can be estimated through a comparison of the redox potentials of the D+/D couples and the energy of the conduction band $E_C = -0.5$ V.

Approximate values[30] of the potentials of the D+/D couples for some of the dyes that exhibited this sensitized reduction current are shown in Fig. 16 in comparison with E_C. This comparison reveals an energy difference between the redox levels and the conduction band 1.2 to 1.7 eV. According to theory[31] the density of the unoccupied D+ levels is described by Eq. (4) with a maximum found at a potential more negative than the D+/D redox level by an amount equal to the rearrangement energy, λ, for the oxidized dye. For these dyes an estimation[2] of λ can be taken to be 0.4 V which indicates that there will be a sufficient density of unoccupied D+ levels at E_C able to accept an electron from the electrode. Reduction of the oxidized dye is possible at the electrode surface in a diffusion controlled siutation. It corresponds, essentially, to a back reaction of the photooxidation reaction.

There is another pathway by which this reduction of the oxidized dye can proceed. The superoxide radical O_2^- which results from reduction of oxygen at the TiO_2 surface, can reduce the oxidized dye which has diffused to the electrode from the bulk of the solution. The resultant molecule may then be reduced once more at the TiO_2 surface yielding a net reaction equivalent to Eq. 7:

$$O_2^- + D^+ \rightarrow O_2 + D$$

$$O_2 + e^- \rightarrow O_2^-$$

At a TiO_2 electrode biased at these potentials it would not be possible to distinguish these two paths for reduction of the oxidized dye.

These pathways for the sensitized reduction reaction explain the regeneration of the dye on the surface which has been oxidized through the photomodulated surface reaction. Fig. 15 reveals that the regeneration during a cathodic polarization sweep does not occur until -0.25 V, a potential at which the dark current reduction of oxygen has become discernible. Thus, the increase in the oxidative photocurrent is intimately tied to the ability of the electrode to donate an electron.

In a DC measurement of the oxidative photocurrent, the regenerative characteristics of Fig. 15 could not be observed. It is possible to detect it through photomodulation only because the rise times of the two currents are so different. These differing rates may be attributed to the small overlap between the conduction band density of states and the D^+ energy distribution (the unoccupied levels of a D^+/D redox couple) as compared with the larger overlap of the conduction band with the D^* distribution (the occupied levels of a D^+/D^* redox couple)[32].

Although several investigations of dye sensitization of semiconductors have utilized photomodulation to aid the detection of the resultant photocurrents, no observation of a sensitized reduction current has been reported. If this reduction current originated from surface states in the band gap of TiO_2, the energy level of this surface state could be no more than 0.3 V positive than the conduction band since the onset of the reduction current is about 0.3 V positive of the flatband potential. This energy difference should not preclude a contribution to the reduction current from the conduction band. Therefore, even if surface states are involved in this reaction, there is no energetic basis for observation of this sensitized reduction reaction at TiO_2 and not at ZnO which has a conduction band energy $E_C = -0.4$ V, very close to that for TiO_2.

This directs attention to the chemical nature of the TiO_2 surface which differs from ZnO. TiO_2 is stable under anodic polarization while ZnO decomposes. Reduction reactions via the TiO_2 conduction band yield different Tafel slopes than the same reactions at a ZnO electrode[25]. Furthermore, Cl^- does not appear to play a significant role in dye sensitized photooxidation at TiO_2 surfaces whereas it does at ZnO. The sensitized reduction current may also be a manifestation of a catalytic characteristic of the TiO_2 electrode.

SUMMARY

A quantum efficiency of 4.0×10^{-3} was measured for electron injection from excited rose bengal into the conduction band of TiO_2. Those few molecules that participate in this reaction must surmount an activation barrier of 6.7 kcals/mole. It was shown that the electron in the excited state rests at a higher energy than the conduction band of the semiconductor. Consequently, this activation energy is thought to originate in the work required to bring the dye molecule close enough to the solid in the proper orientation so that electron transfer may occur. These reactive molecules are probably adsorbed on the surface at sites which possess heats of adsorption greater than the 7.6 kcals/mole measured for the bulk of the dye on the surface.

The majority of the rose bengal on the surface is most likely adsorbed at non-reactive locations. Upon excitation these dye molecules can be oxidized by the oxygen generated at the electrode; they can also transfer this energy to neighboring molecules through a weak Forster energy transfer mechanism. In this manner the dye on reactive sites need not directly adsorb the incident radiation in order to inject an electron into the TiO_2. As a result, the quantum efficiency of electron transfer remains constant as the surface population of the dye increases.

At negative bias potentials the surface electron concentration in the conduction band is high enough to donate an electron to oxidized dye molecules on the surface and in the solution. The oxidized dye can be created through the photo-injection of electrons into the electrode or through oxidation by oxygen. The reduction current was observed for dyes other than rose bengal.

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Table 1. Calculated values for the rose bengal adsorption isotherms of Fig. 2.

	21.5^{o}		36.5^{o}
$1/C_m$	$4.57 \times 10^{6} \pm .07$	$cm^{2}/mmole$	$4.87 \times 10^{6} \pm .04$
$1/C_mK$	$27. \pm 13$	cm^{2}/ml	$41. \pm 7$
C_m	$2.19 \times 10^{-7} \pm .04$	$mmole/cm^{2}$	$2.05 \times 10^{-7} \pm .02$
$1/K$	$6 \times 1^{-6} \pm 3$	$mmole\ cm^{3}$	$8 \times 10^{-6} \pm .02$
Area	75	$A^{2}/molecule$	81
ΔH	7.3-7.9	kcal/mole	7.5-7.7

FIGURE CAPTIONS

Fig. 1. Experimental set-up is shown for measurement of sensitized photocurrents at semiconductor electrodes. White light from a Xe high pressure lamp was modulated by a mechanical chopper and monochromatized with either a monochromator or interference filter. Photocurrent produced at the TiO_2 surface was amplified by a current to voltage converter and then fed to a lock-in amplifier. The crystal bias was controlled by a potentiostat with the aid of a function generator, a sat'd calomel reference electrode, and a Pt counterelectrode.

Fig. 2. Adsorption isotherms of rose bengal on TiO_2 single crystals were determined by an elution method at two temperatures, 21.5° C —— and 36.5° C---. A plateau was attained at 2.14×10^{-7} mmoles/cm^2 for 21.5° C and at 1.95×10^{-7} mmoles/cm^2 for 36.5° C. The dye solutions were 1 M in KCl.

Fig. 3. Absorbance spectra of rose bengal adsorbed onto TiO_2 single crystals are shown for different surface concentrations. (a) 0.98×10^{-7} (b) 1.19×10^{-7} (c) 1.73×10^{-7} (d) 2.13×10^{-7} mmoles/cm^2. These spectra are the sum of the absorbances of six surfaces.

Fig. 4. The solution absorbance of rose bengal in 1 M KCl reveals increasing dimer formation over the range of dye concentrations covered by the adsorption isotherm of Fig. 2. Spectrum (a) represents the monomer form with a higher energy shoulder 30 nm down from the maximum at 540 nm. Spectrum (c) shows the emergence of the dimer maximum at 520 nm. These spectra correspond to dye concentrations of (a) 5.4×10^{-5} M (b) 2.1×10^{-4} M, (c) 4.4×10^{-4} M.

Fig. 5. (a) The time decay of rose bengal sensitized photocurrents at TiO_2 reveals an initial fast decay with a subsequent slow decrease in the rate of photooxidation. 560 nm light was used with a 3.6 hz modulation and a 0.0 V bias (vs. SCE). Dye concentration was 4.38×10^{-4} M. (b) At a bias of -0.50 V the photocurrent is noiser but does not decay from its initial level.

Fig. 6. (a) Photocurrent produced by defects in the crystal itself decreased with increasing wavelength. This serves as a baseline for the sensitized oxidative photocurrent (b) that occurs when the dye is adsorbed onto the electrode surface. This action spectrum was taken when the photocurrent had reached a decay level equivalent to point A in Fig. 5. The bias was 0.18 V (SCE). Dye concentration was 4.38×10^{-4} M.

Fig. 7. Although chloride functions as a reducing agent for excited dyes on the surface of ZnO, it can be seen here that chloride does not affect the quantum efficiency of charge transfer from rose bengal to TiO_2 over a concentration range of .08 M to 1.0 M.

Fig. 8. The photocurrent produced by rose bengal at TiO_2 electrode increases with increasing solution concentration of the dye until a plateau is attained at about 1.0×10^{-4} M. Illumination was at 560 nm with a 0.0 V bias (SCE). Each point in this curve represents the average of the initial values of five photocurrent measurements.

Fig. 9. The quantum of electron transfer was found to be independent of the surface concentration of the dye down to about 40% coverage of the electrode. This graph was constructed from data like those depicted in Figs. 3 and 8. $\theta = 1.0$ corresponds to a surface coverage of 2.2×10^{-7} mmoles/cm^2.

Fig. 10. (a) A logarithmic analysis of the photocurrent as a function of pH yielded a line with an average slope of .07 ± .01. (b) The pH of the solution affects the photocurrent because of the pH dependent adsorption characteristics of the dye. From a basic electrolyte less dye is adsorbed on the surface than from neutral or acidic solutions. A slope of .07 ± .01 was also found for this measurement.

Fig. 11. An Arrhenius plot of the quantum efficiency of Eq. (2) for photo-oxidation of rose bengal yields an activation enthalpy of 6.7 ± .5 kcal/mole. Each data points represents a single experimental measurement; illumination was at 560 nm with a 0.20 V bias on the electrode. The rose bengal concentration was 1.6 x 10^{-4} M. The pre-exponential factor was 4 x 10^3.

Fig. 12. The commonly observed dependence of dye sensitized photocurrent on electrode bias is shown here for rhodamine B at a ZnO electrode. In an anodic polarization sweep of 5 mV/sec, the current rose from zero at cathodic potentials to saturation at about 0.20 V (SCE). The current-voltage measurement in this figure was taken after the photocurrent had reached a steady state decay rate equivalent to point A in Fig. 6. Illumination was at 565 nm; concentration of the dye was 2.0 x 10^{-4} M. The potential dependence of the initial undecayed photocurrent is qualitatively identical, but with a much larger saturation value of the current.

Fig. 13. The current-voltage behvior of rose bengal sensitized TiO_2 displays some unusual features. (a) oooo Here the magnitude of the initial, undecayed anodic photocurrent is plotted as a function of specific bias potentials (b) ---- If the current is first allowed to decay at 0.0 V bias (SCE), a cathodic sweep restores the anodic current to its maximum at about -0.50 V. (c) ——The common cathodic behavior of both (a) and (b) is a reduction current

which peaks at about -0.85 V. The decrease at more cathodic polarization is due to H_2 evolution. Note the change in scales for the cathodic current. 3.6 hz modulation was used with 560 nm illumination; concentration of the dye was 5 x 10^{-5} M. The sweep rate was 5 mV/sec.

Fig. 14. Maintaining the TiO_2 bias at -0.49 V, which corresponds to the anodic peak of Fig. 12b, the photocurrent measured for one period of the chopping cycle revealed different time scales for the oxidation and reduction reactions. In (a) a 3.6 hz chopping frequency yielded anodic and cathodic currents of equal magnitude but with different rise times. In (b) the modulation is decreased by ten. With increased time of exposure to illumination the reduction current predominates. A signal averager was used to obtain these results.

Fig. 15. A number of reactions can occur at a negatively biased TiO_2 electrode. (a) The cathodic sweep of the dark current reveals reduction of oxygen at the surface (-0.25 V) followed by hydrogen evolution (-0.80 V). (b) The potential range over which oxygen is evolved is shown through measurement of the intrinsic photocurrent produced by illumination at λ = 390 nm. The 390 nm light was modulated at 11.0 hz. (c) The dye sensitized oxidized oxidation and reduction behavior of Fig. 13b is included for comparison.

Fig. 16. An analysis of the energetics of a dye-semiconductor pair is presented here. The ordinate represents an energy scale with the abscissa providing a measure of the density of states of the semiconductor and a distribution function for the dye as expressed by Eq. (4). The lowest level of the conduction band is labeled E_C with the means of the ground and excited state distribution of the adsorbed dye labeled E_D and E_D*. The reduction potential for the solution dye, E_R, yields a value for E_D^{*sol}. This distribution is placed on a scale with the estimates of the oxidation potentials, D^+/D, of some of the dyes which sensitized the photoreduction at TiO_2: rose bengal (RB), acridine orange (AO), thionine (TH).

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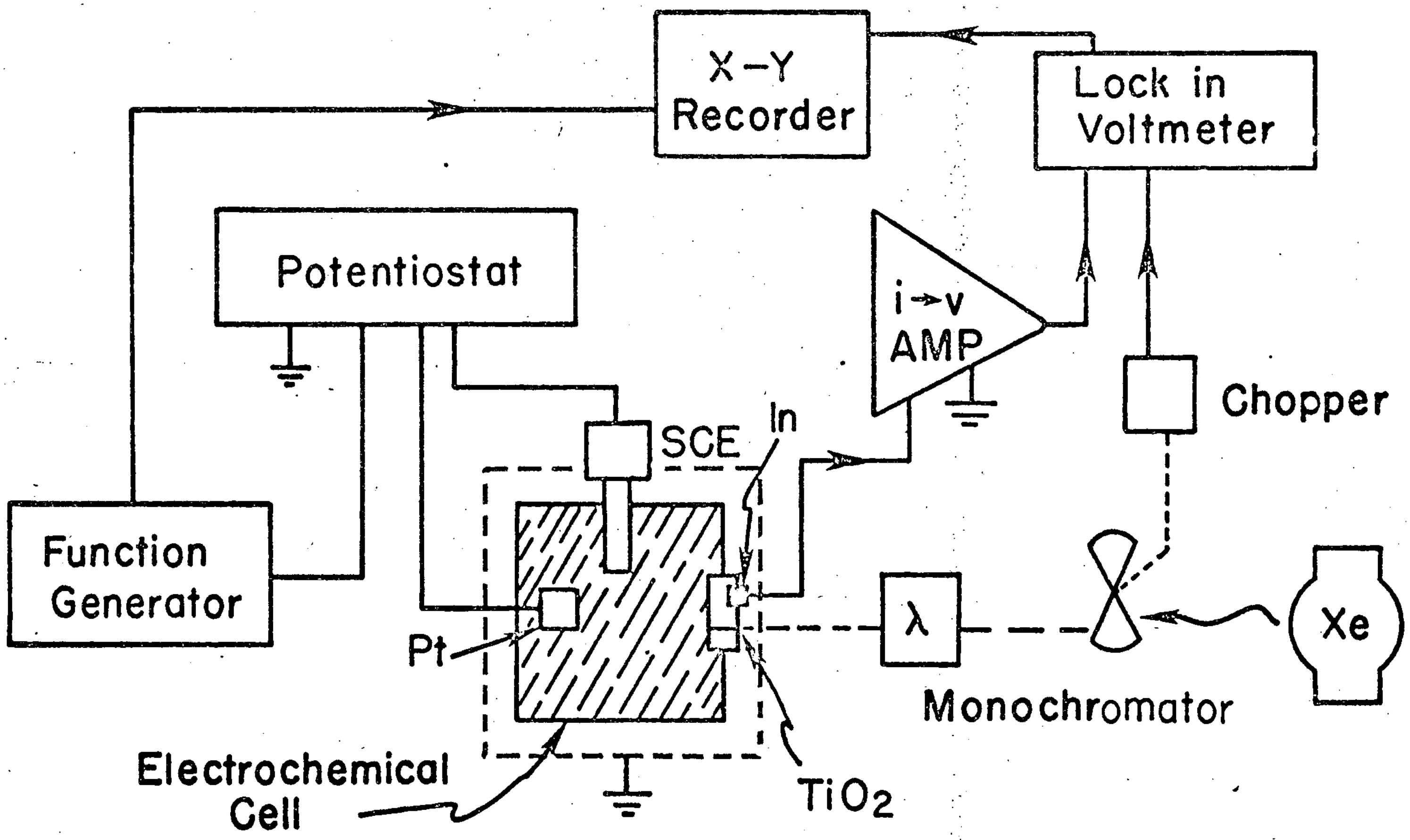

XBL 767-6064

Fig. 1

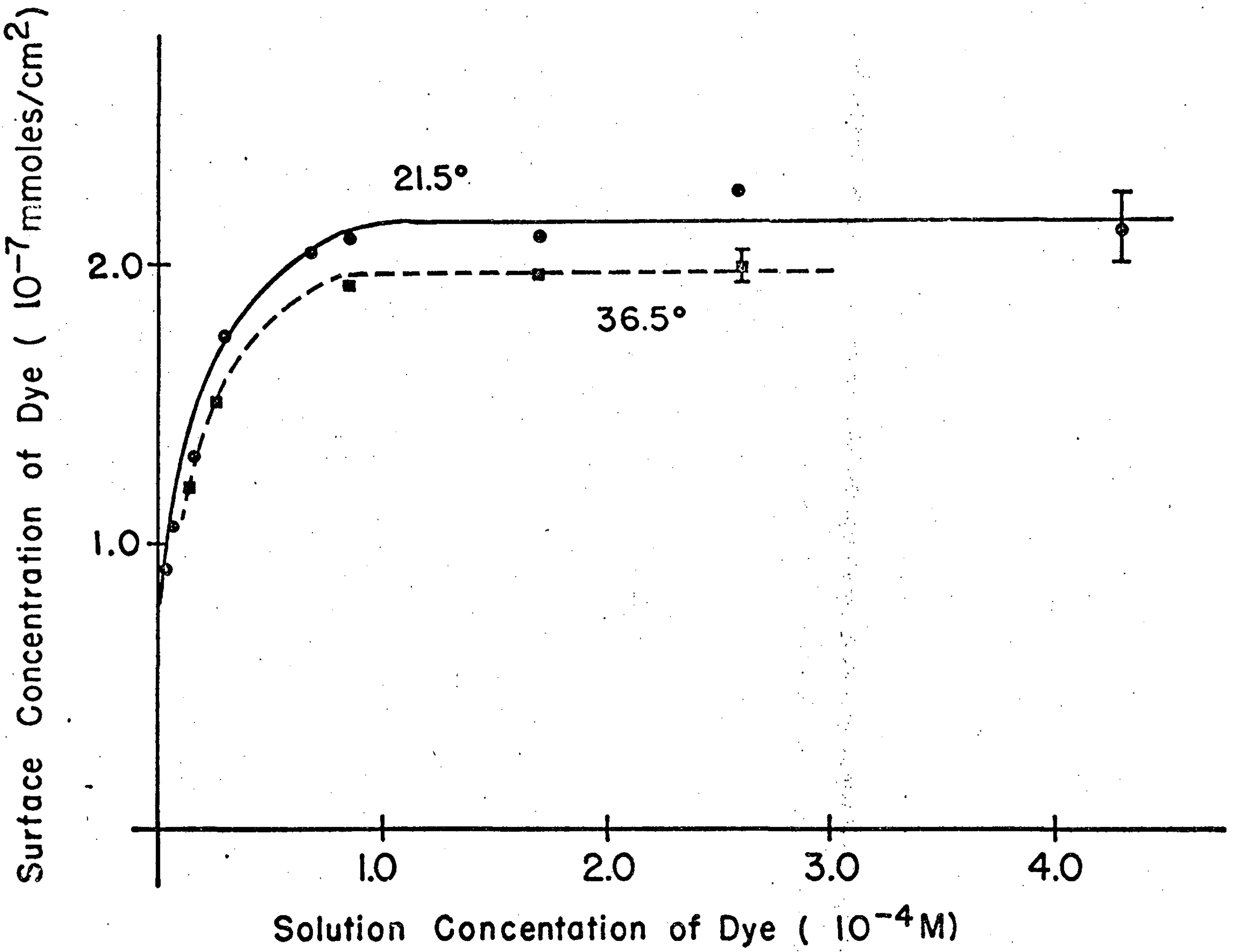

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Fig. 2

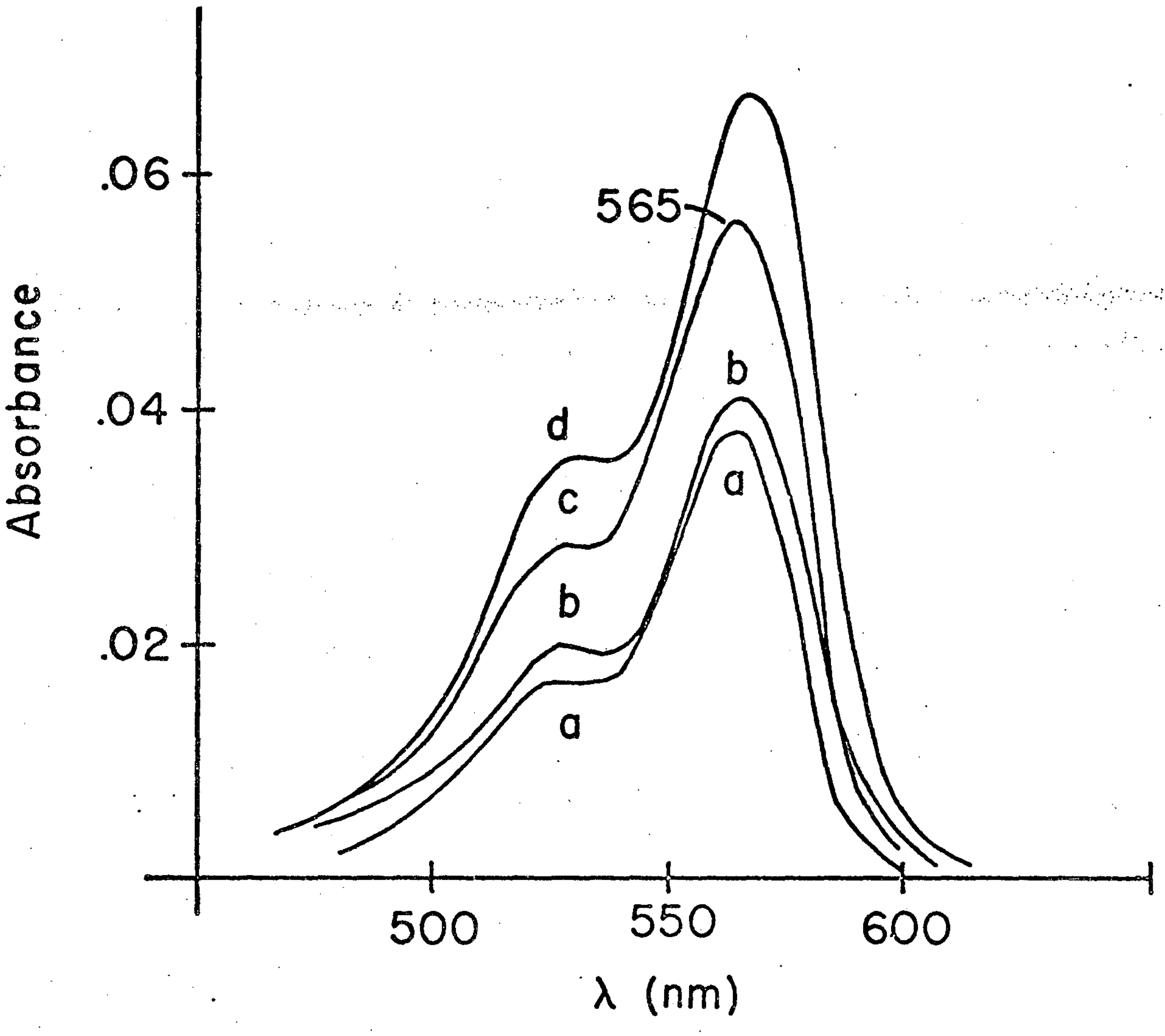

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Fig. 3

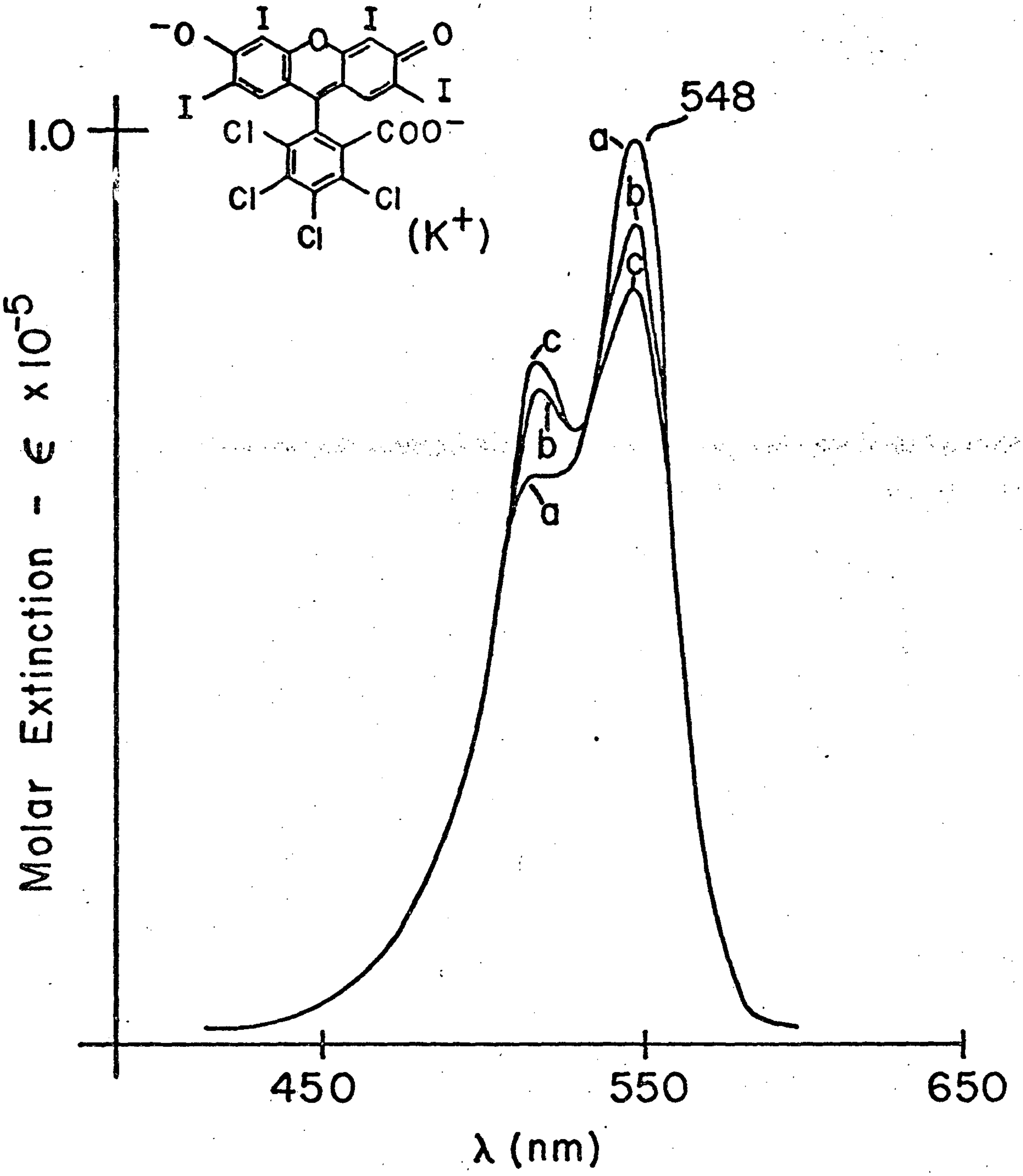

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Fig. 4

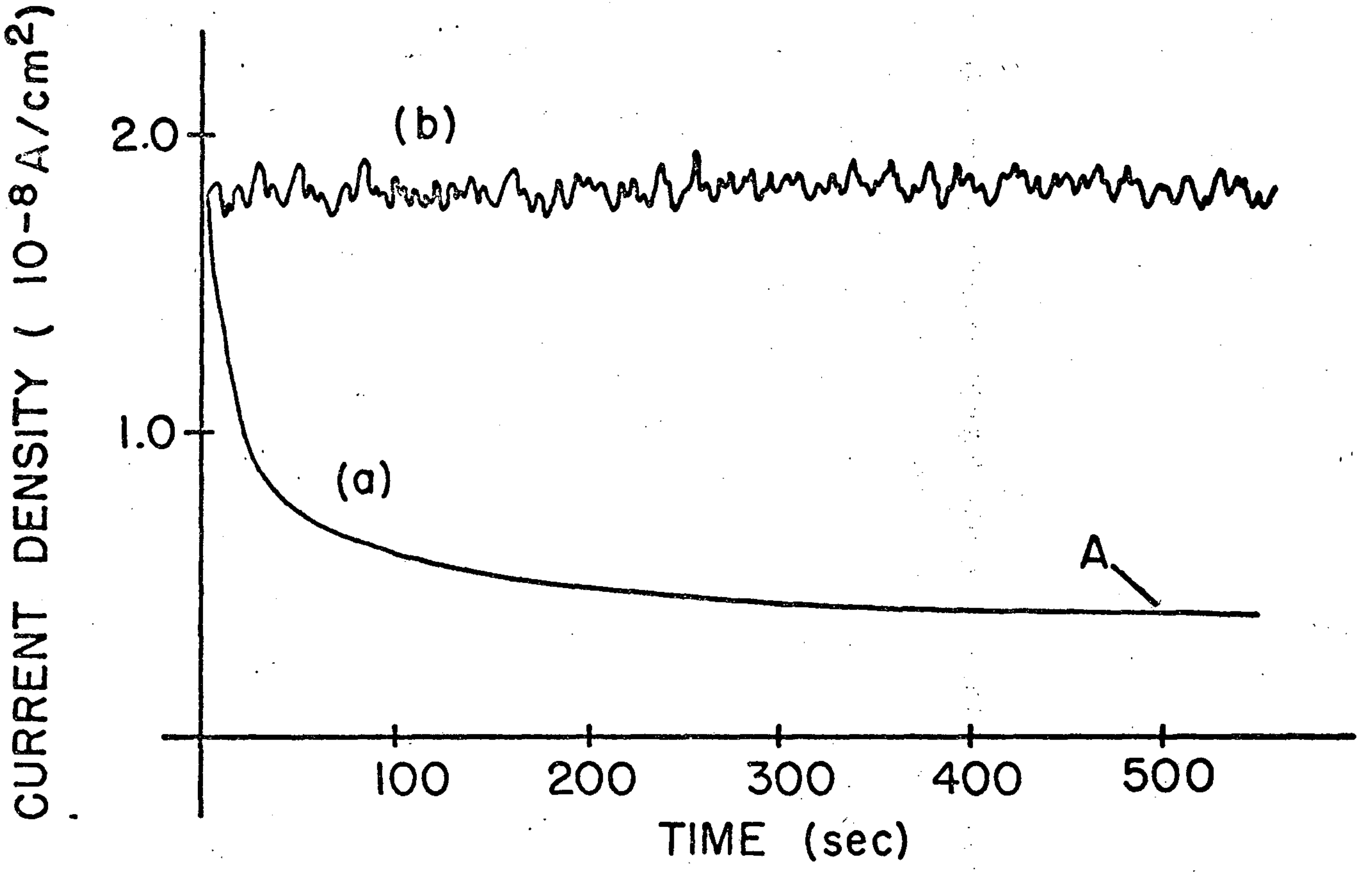

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Fig. 5

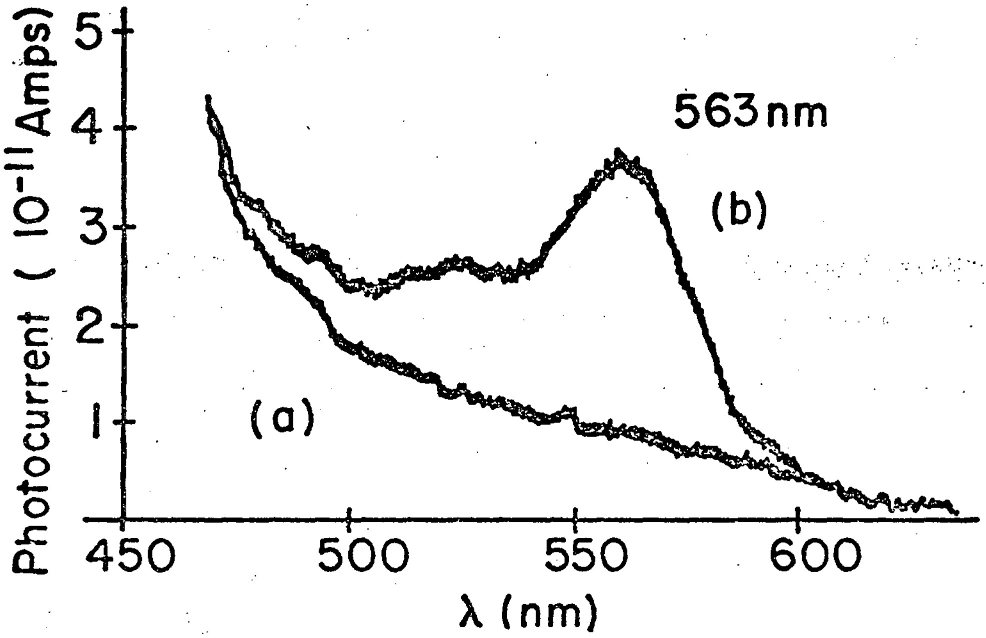

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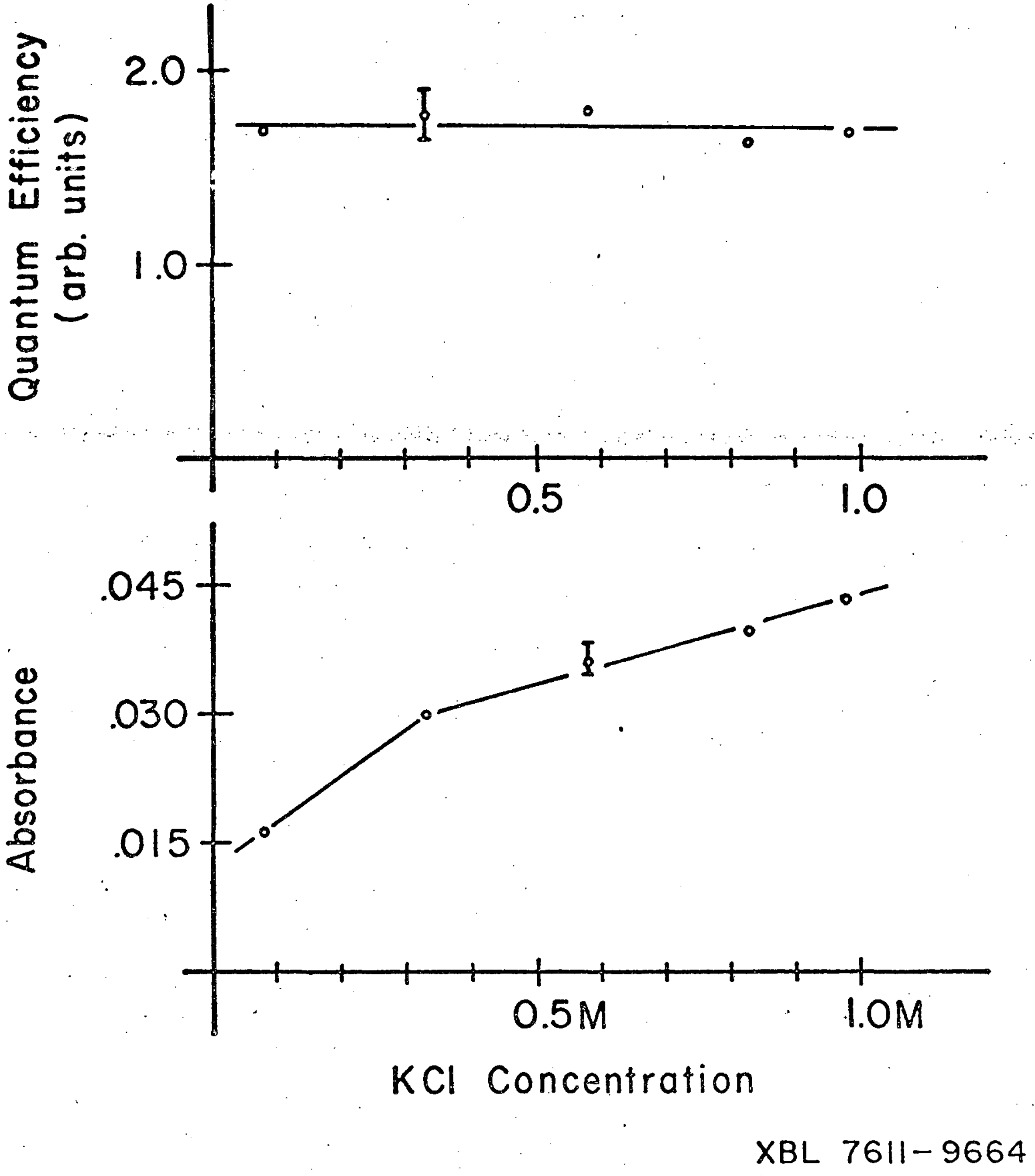
Fig. 6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1.0
Absorbance
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1.0M
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XBL 7611-9664

Fig. 7

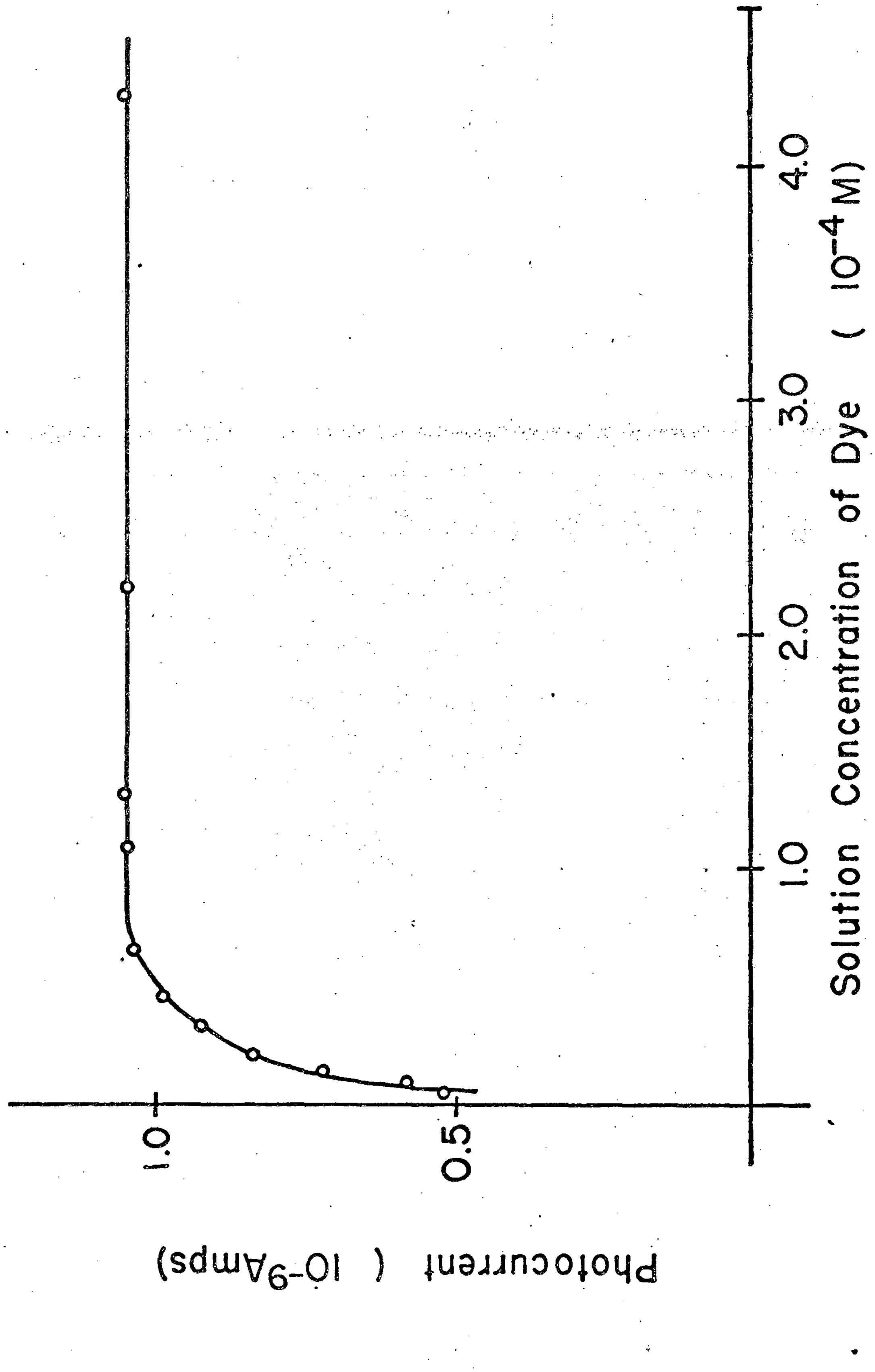

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Fig. 8

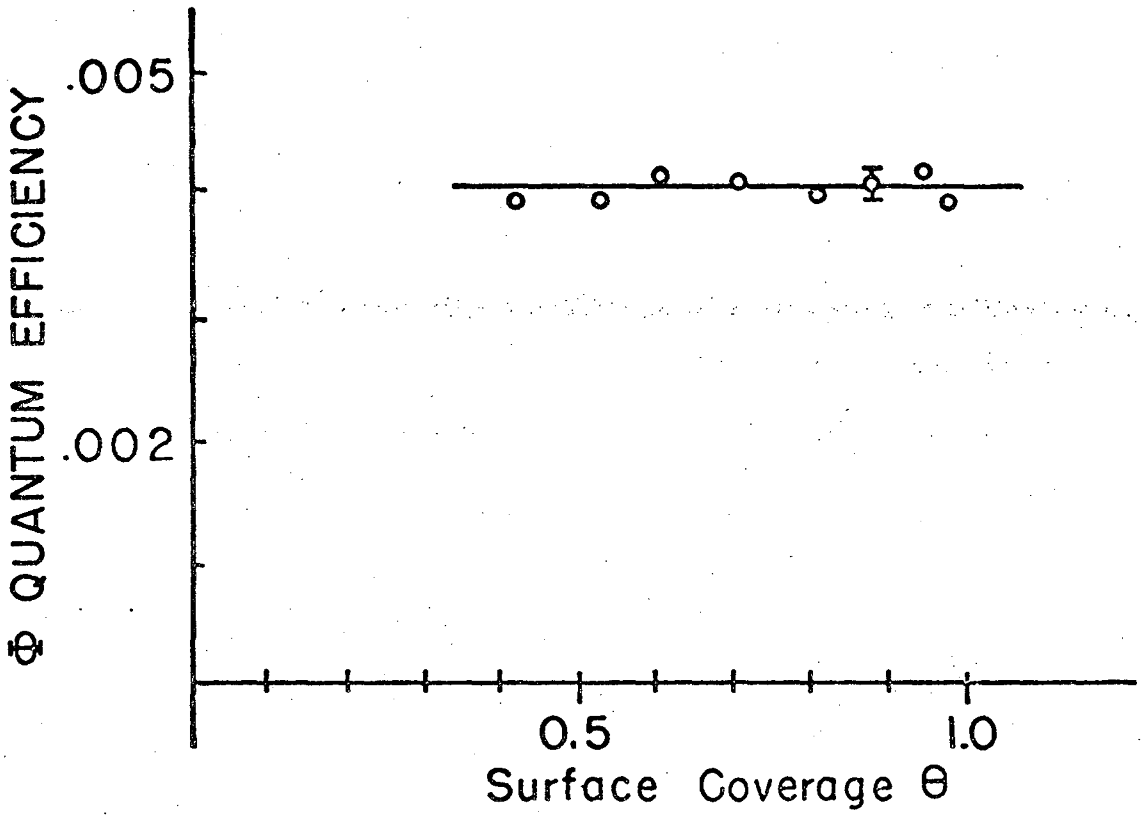

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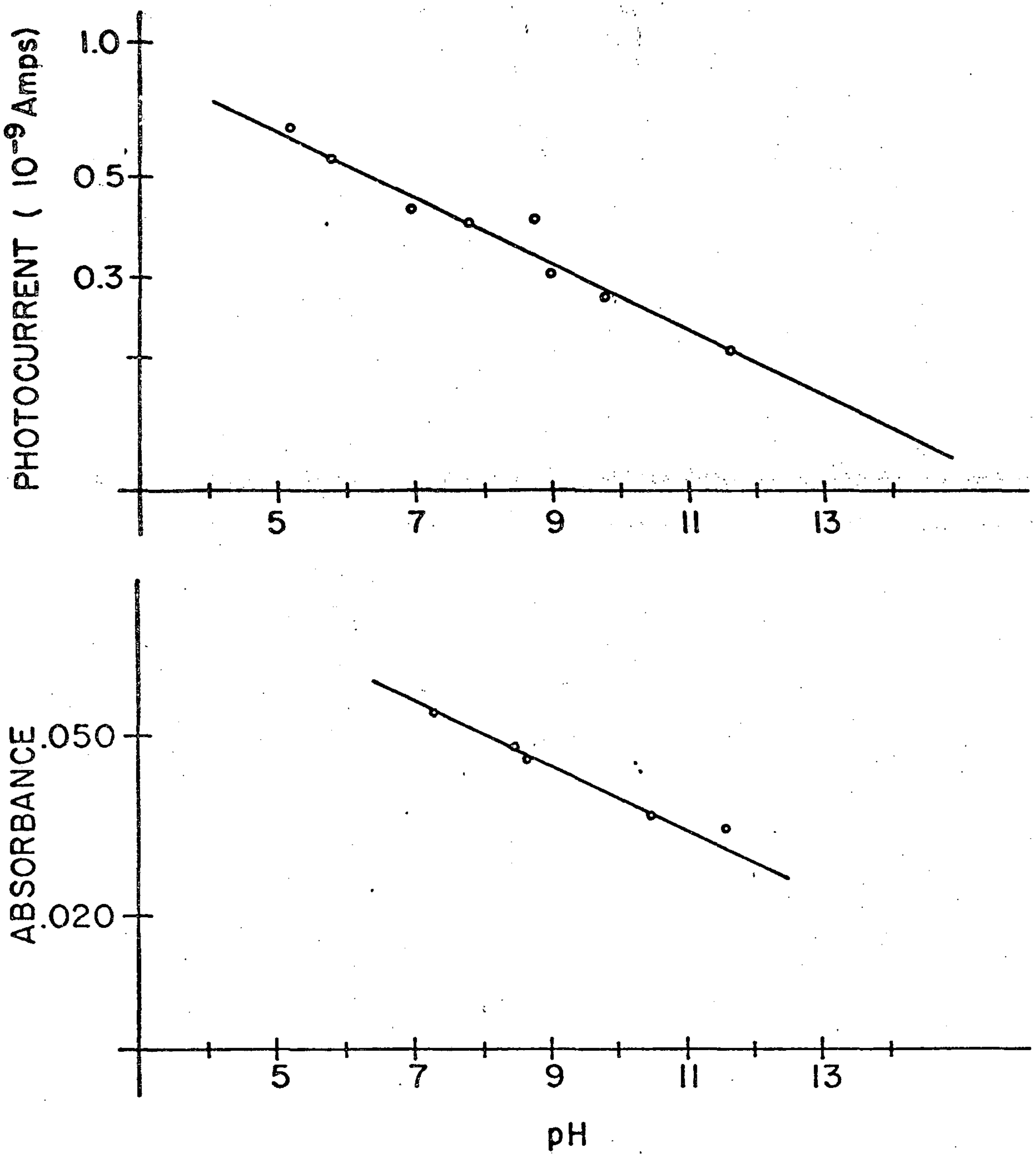
Fig. 9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0.5
0.3
5
7
9
11
13
ABSORBANCE
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.020
5
7
9
11
13
pH
XBL 767-6059 A

Fig. 10

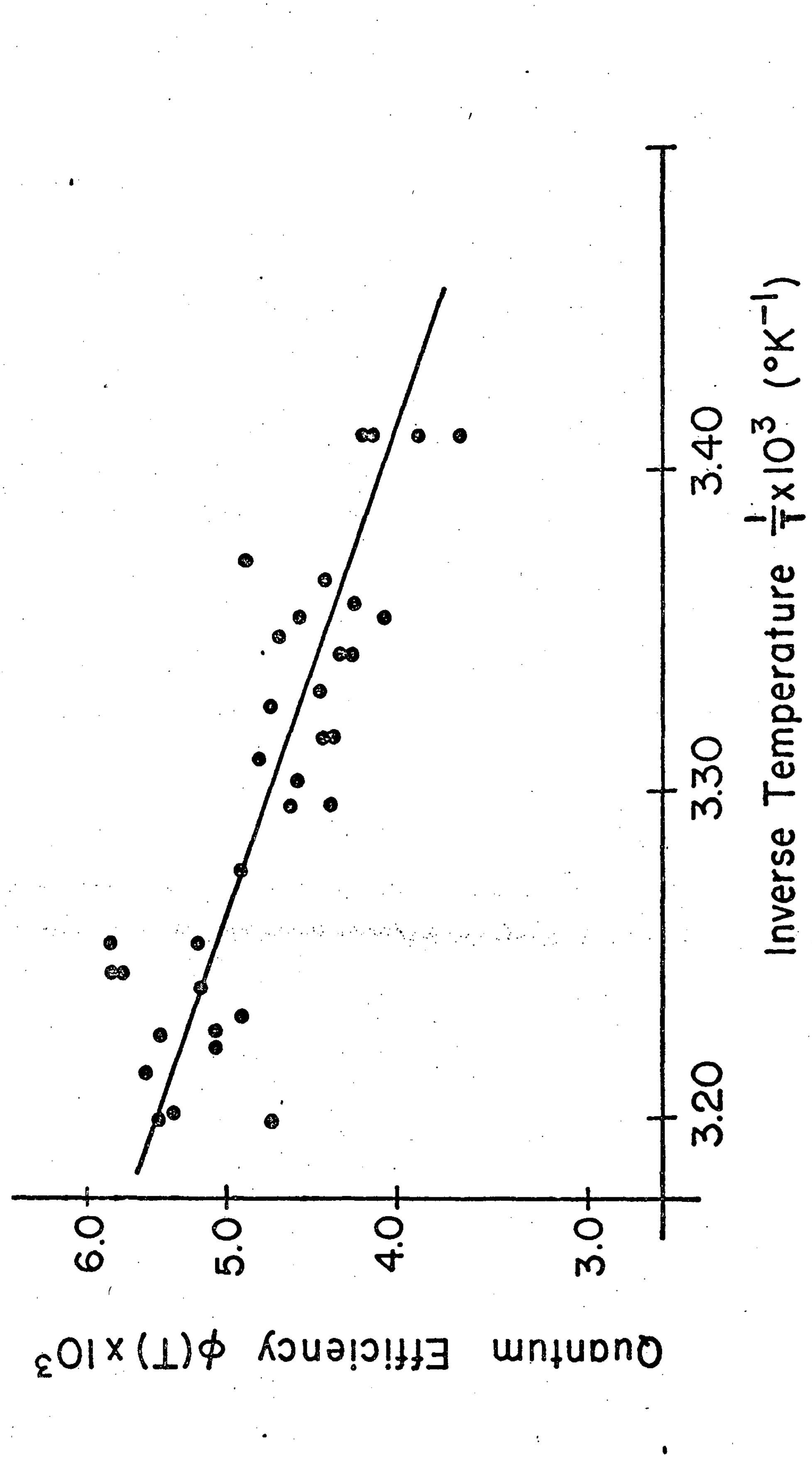

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Fig. 11

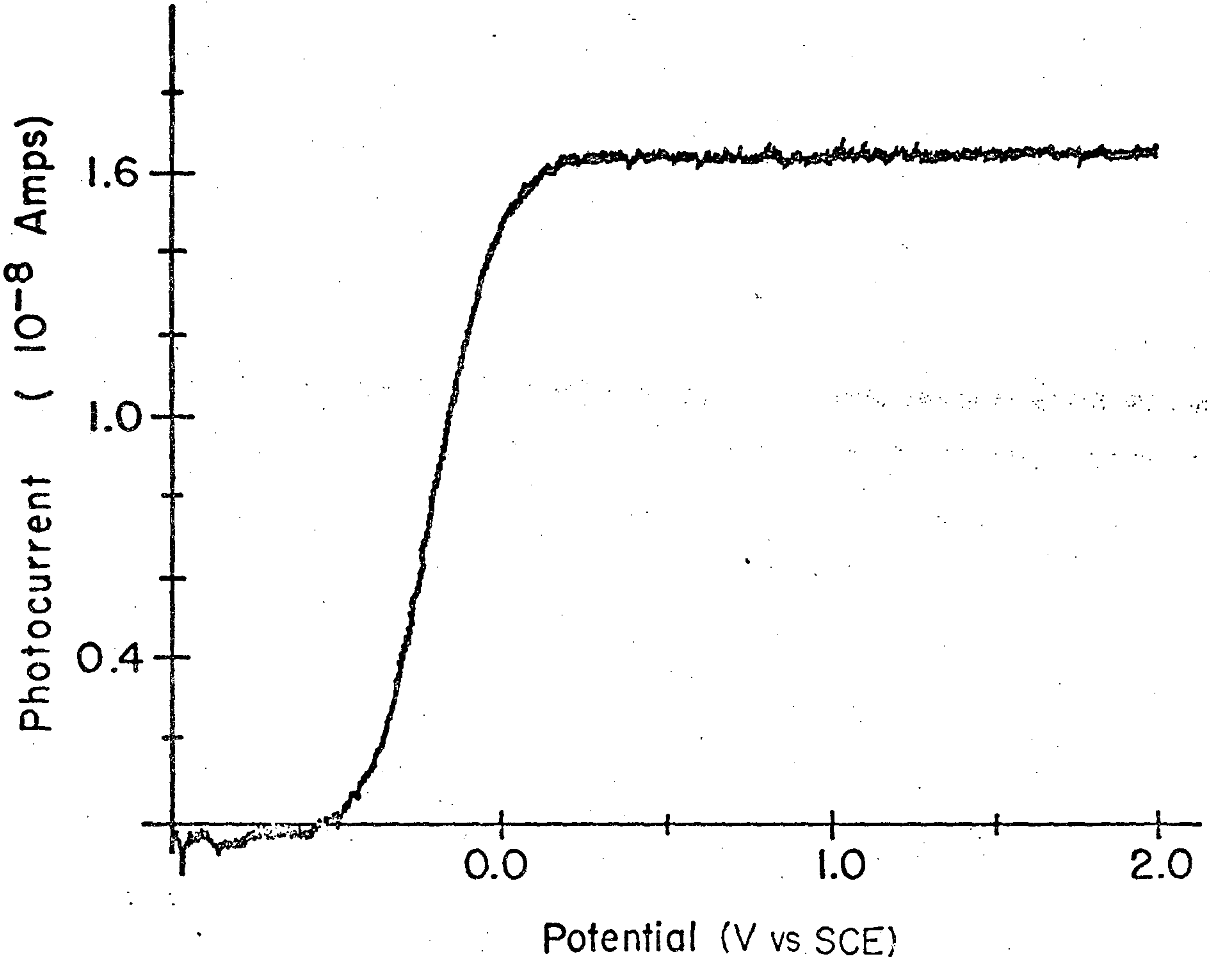

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Fig. 12

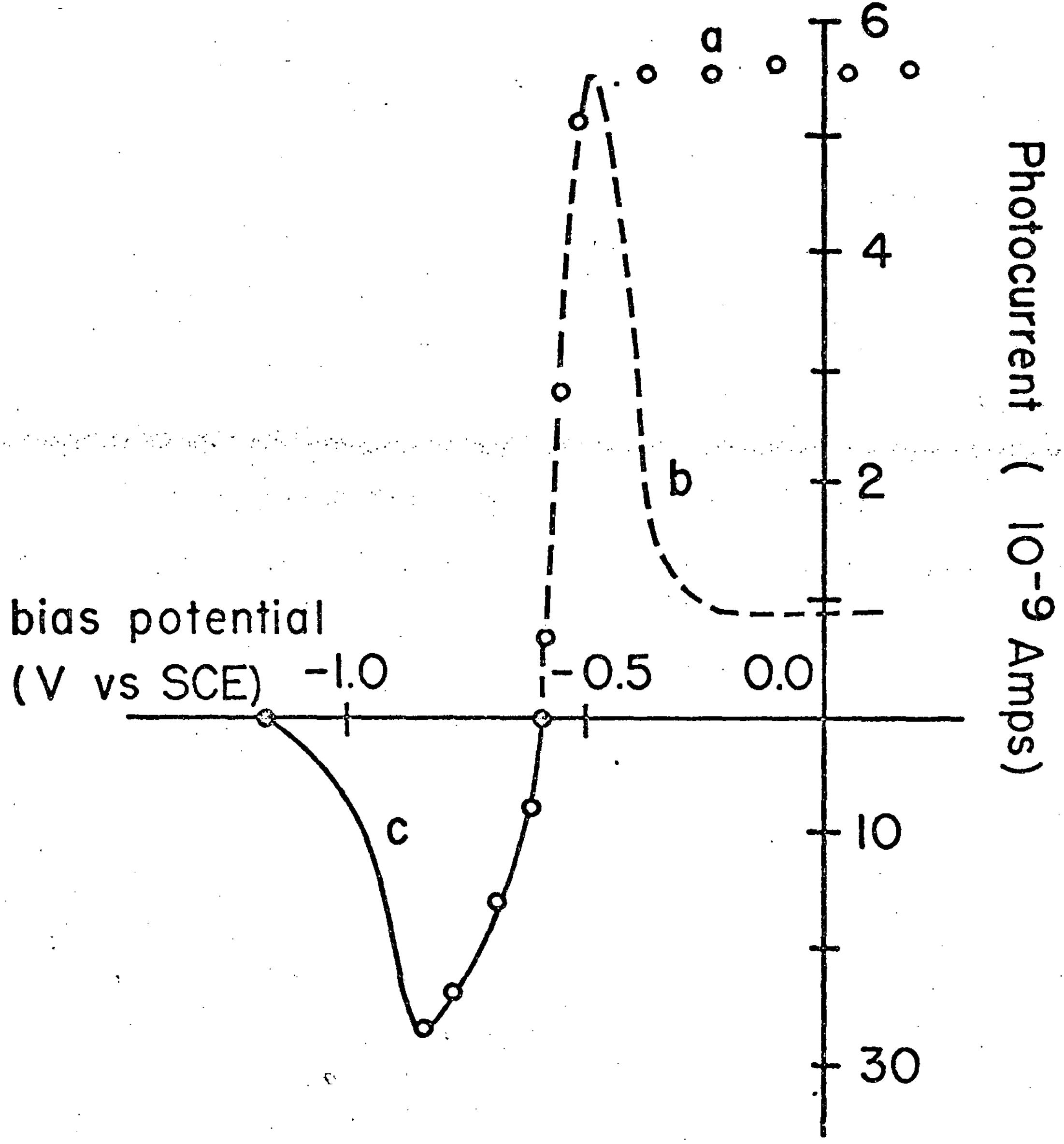

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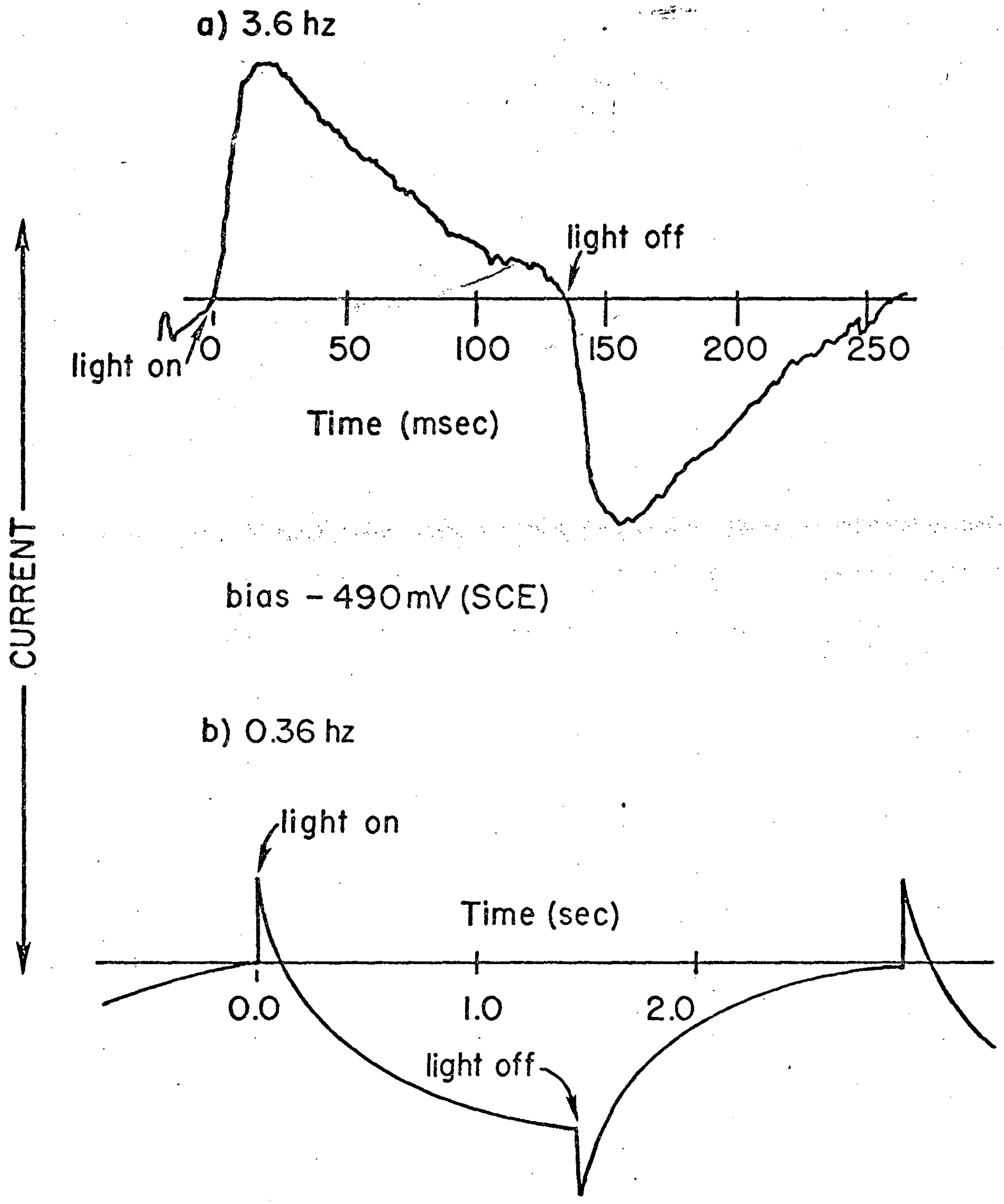
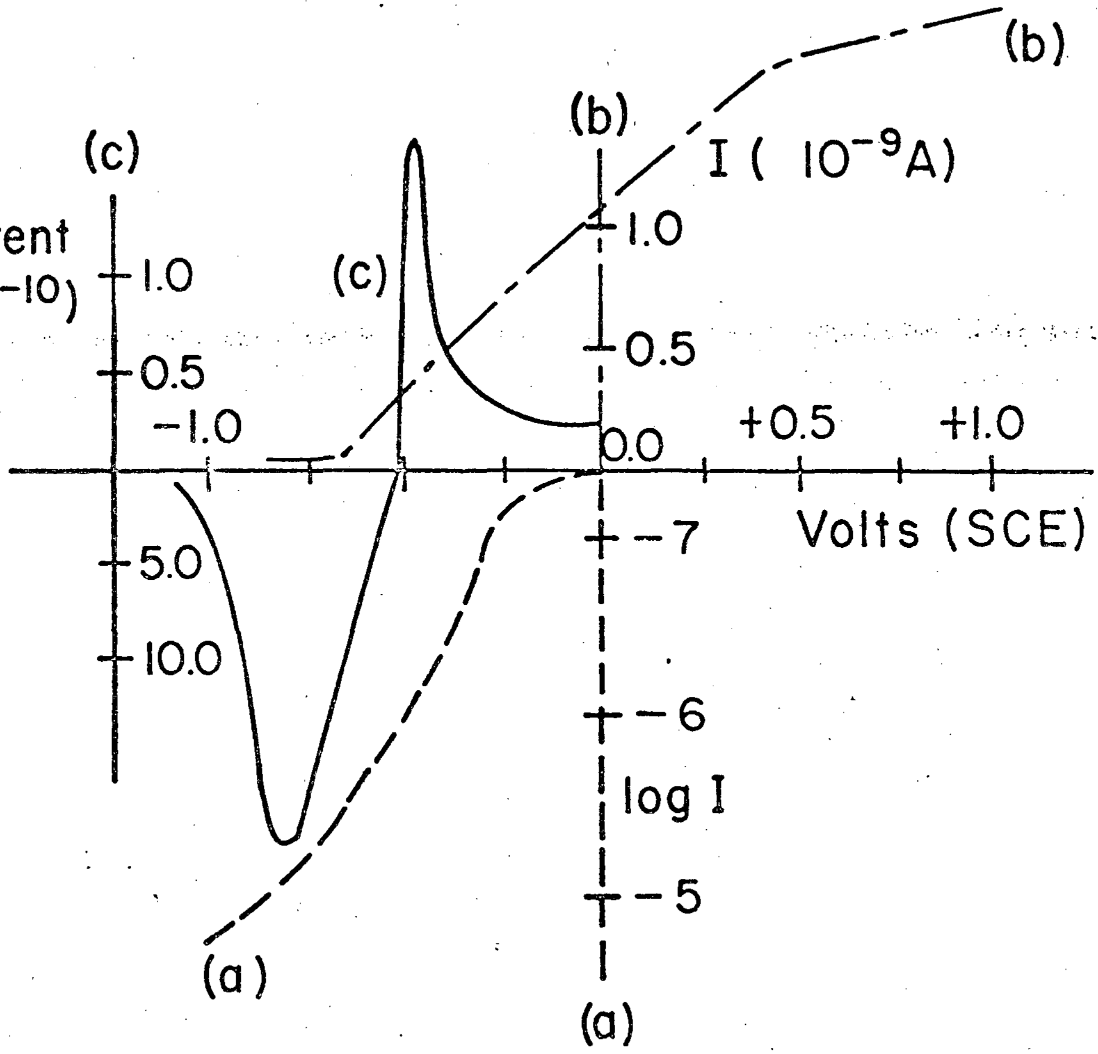
Fig. 13



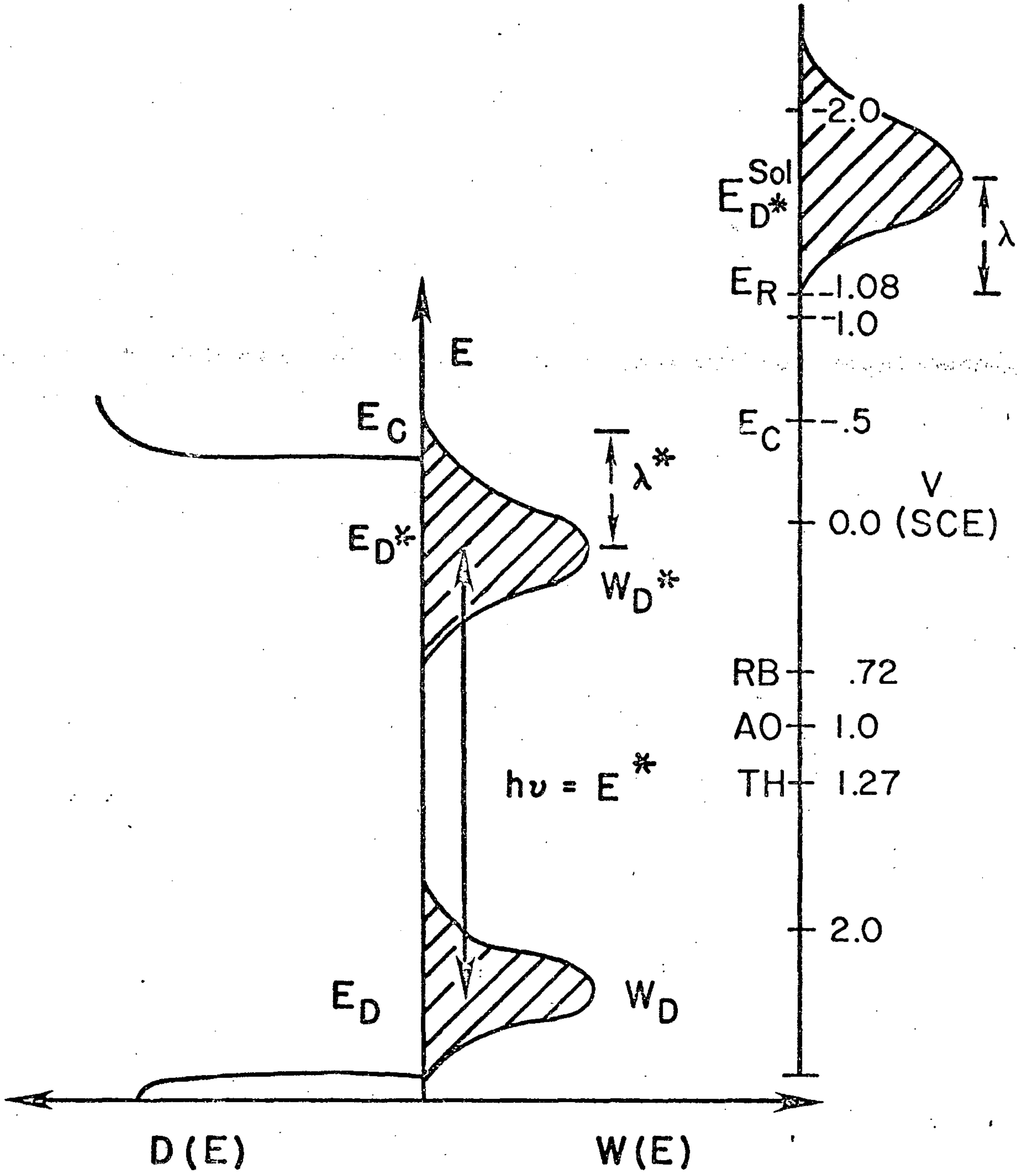
XBL 767-6057

Fig. 14



XBL 7611-9665

Fig. 15



XBL 767-6056A

Fig. 16

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