Chapter 3

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3.1 Electrochemical methods.

Various electrochemical techniques have been employed to extract useful informations from the molecules object of this study. Usually electrochemical methods are of fundamental importance in evaluating the potential of a redox couple, the kinetics of the heterogeneous electron transfer and the reversibility of the electrodic processes. Useful information about the diffusion coefficient of an electroactive specie can also be obtained from a variety of controlled potential experiments. Figure 39 is a picture of the basic experimental system. A potentiostat has control of the voltage across the working electrode-counter electrode pair, and adjusts this voltage to maintain the potential difference between the working and the reference electrodes (through a high impedance feed back loop) in accord with the program defined by a function generator.

![Experimental arrangement for controlled potential experiments.](image)

3.1.1 Chronoamperometry

The usual observable in controlled potential experiments are currents as functions of time and potential. If the potential is stepped to the mass transfer controlled region, the concentration of the electroactive specie is nearly zero at the electrode surface and the current is totally controlled by the mass transfer. Regardless if the kinetics of the electrodic process are basically facile or sluggish, they can be activated by a sufficiently high potential (unless the solvent or the supporting electrolyte are oxidized or reduced first). This condition will hold at any more extreme potential.

Considering a planar electrode (e.g. a Pt disk) and an unstirred solution it can be shown that the current-time response is given by:
which is known as the Cottrell equation
\[ i_d = \frac{nFAD^2C^*}{\pi^{1/2}t^{1/2}} \] (3.1)
which is known as the Cottrell equation 73. Its validity was verified in detail by Kolthoff and Laitinen74,75, who measured and controlled all parameters (number of exchanged electrons, electrodic area, diffusion coefficient and bulk concentration of the electroactive specie). Thus the diffusional current is linear with respect to the inverse of \( t^{1/2} \). From the slope it is possible, for example, to calculate \( D \), knowing all the other experimental parameters. In practical measurements under Cottrell conditions one must be aware of different instrumental and experimental limitations: equation (3.1) predicts large currents at short times, but the actual maximum current may depend on the current-voltage output of the potentiostat. In addition during the initial part of the current transient, the recording device may be overdriven and some time may be required for recovery. A non faradic current which decays with a constant time given by \( R_uC_d \), where \( R_u \) is the cell uncompensated resistance and \( C_d \) is the double layer capacitance, also flows during a potential step. So for a period of about 5 time constants an appreciable contribution of the charging current to the total measured current exists. Figure 40 is an example of the waveform used for a potential step experiment and of the resulting current-time response.

![Figure 40](image)

**Figure 40** (a) waveform for a step experiment in which the electroactive specie is electroinactive at \( E_1 \) but is reduced at the diffusion limited rate at \( E_2 \). (b) Concentration profiles for various times of the experiment. (c) Current flow vs.time.

73 F. G. Cottrell Z. Physik. Chem. 1902, 42, 385
3.1.2 Steady state voltammetry

In conception sampled current voltammograms involve the recording of an $i(\tau)$-E curve by application of a series of steps to different final potentials $E$. The current is then sampled at a fixed time $\tau$ after the step, then $i(\tau)$ is plotted vs $E$. Usually the initial potential is chosen to be to a constant value where no faradic process occur. For example, as depicted in figure 41 at potential 1 there is no faradic current, while at potential 2 and 3 the faradic process occurs but not so effectively that the surface concentration of the electroactive specie is zero. At potentials 4 and 5 we obtain the same current determined by the mass transport of the redox specie from the bulk of the solution to the electrodic surface. Actually in the common practice one does not even need to apply steps. It is satisfactory to change the potential linearly with time and to record the current continuously, as long as the rate of change is small compared to the rate of adjustment of the steady state.

![Figure 41. Sampled current voltammetry: (a) Step waveforms applied in a series of experiments. (b) current time curves observed in response to the steps. (c) Sampled current voltammogram.](image)

The shape of the voltammogram obtained for a reversible system in sampled current voltammetry is described by the following equations:

\[
E = E^0 + \frac{RT}{nF} \ln \frac{D_k^{1/2}}{D_O^{1/2}} + \frac{RT}{nF} \ln \frac{i_a - i}{i}
\]  
(3.2)
When \( i = i_d/2 \) the current ratio becomes unity so that the third term vanishes. The potential for which it is so is \( E_{1/2} \) and it is called the half wave potential.

\[
E_{1/2} = E^0 + \frac{RT}{nF} \ln \frac{D^{1/2}_d}{D_0^{1/2}}
\]  

(3.3)

Usually (3.2) is often written as:

\[
E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_d - i}{i}
\]  

(3.4)

As shown in figure 42 these relations predict a wave that rises from baseline to the diffusion controlled limit in a fairly narrow potential region (about 200 mV) centred on \( E_{1/2} \). Since the ratio of diffusion coefficients in (3.3) is nearly unit in almost any case, \( E_{1/2} \) is usually a very good approximation to \( E^0 \) for a reversible couple.

![Figure 42. Characteristics of a reversible wave in sampled current voltammetry.](image)

For a reversible system the wave slope from (3.4) should be about \( 60/n \) mV. Larger slopes are generally found for systems that do not have both nernstian heterogeneous kinetics and overall chemical reversibility; thus the slope can be used to diagnose reversibility. In addition, for a simple one step \( O + n(e) \rightarrow R \) reaction, from the steady state voltammogram, one can obtain current-overpotentials values useful for determining the exchange current
density, according to the low field approximation of the Butler and Volmer equation\(^\text{76}\). It is in fact possible to show that the current is linearly related to overpotential in a narrow potential region in the immediate proximity of the equilibrium potential. In contrast with reversible cases just examined, in quasi-reversible cases the electron transfer kinetics of the system are not so fast to instantaneously adjust to the new electrodi-potential, in other words the concentration of the oxidized and reduced species at the electrodi-surface cannot be satisfactory described by the Nernst equation at that determined potential. Kinetic parameters like the electron transfer rate constants and the transfer coefficients influence the response to potential steps and can often be evaluated from those responses. Usually working curves\(^\text{77}\) or computer programs are used to simulate these curves and to obtain the parameters of interest.

### 3.1.3 Cyclic voltammetry

Cyclic voltammetry has become a very popular technique for initial electrochemical studies of new systems and has proven very useful for obtaining informations about fairly complicated electrodi-reactions. A typical linear sweep voltammetry for a system like anthracene is shown in figure 43. If the scan is begun at a potential well positive of \(E^0\) only capacitive current flows until in the vicinity of the \(E^0\) the reduction begins and the faradic current starts to flow. As the electrode potential continues to grow more negative the current increases until the surface concentration of the electroactive specie drops nearly to zero, the mass transfer of anthracene to the surface reaches a maximum rate and then it declines as the depletion effect sets in. The observation is therefore a peaked current – potential curve like that depicted.


If at some point we reverse the potential scan, we approach and then pass $E^{0'}$ sweeping in a positive direction and consequently the radical anion that has been generated during the forward scan, present in large concentration in the vicinity of the electrode becomes reoxidized and an anodic current flows. This reversal current has a shape much like that of the forward peak for essentially the same reasons (Figure 44).

Parameters of interest obtainable from cyclic voltammograms are obviously the half wave potential, which is related to $E^{0'}$ by a relationship previously described (3.3) and can be easily calculated form the average of anodic and cathodic peak potentials, the peak separation and the peak current. In case of an ideally Nernstian electrochemical process the peak separation should be of the order of $60/n$ mV, in addition the half wave potential and the peak separation should be independent from the scan rate. Deviations from this behaviour are

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**Figure 43** (a) Linear potential sweep starting at $E_i$. (b) Resulting i-E curve. (c) Concentration profiles of the oxidized and reduced species.

**Figure 44.** (a) Cyclic potential sweep. (b) resulting cyclic voltammogram
usually determined by sluggish electron transfer kinetics of the system under study or to other kinetic complications. In case of a diffusion-limited electrodic process the peak current should be linearly related to the square root of the scan speed according to equation (3.5):

\[
I_p = (2.69 \times 10^5) n^{3/2} AD^{1/2} C_v^{1/2}
\]

For a Nernstian wave with a stable product the ratio between the anodic and cathodic peak should be unitary, regardless of the scan rate and diffusion coefficient. Deviations from unity are indicative of coupled homogeneous chemical reactions or complications in the electrodic process. If the electrochemical response is given by a specie adsorbed on the surface of the electrode the peak current is proportional to the scan speed, providing a powerful tool to discriminate between electrochemical processes originated by species diffusing to the electrodic surface from the solution or, on the contrary, directly adsorbed on the electrode. In case of quasi reversible couples the peak separation is a function of \( v \), \( k_0 \) and \( \alpha \). It has been developed a method (often called the method of Nicholson)\(^{78}\) useful for estimating the electron transfer constant \( k_0 \) based on the determination of the peak separations at various scan speeds, from which it is possible, with the aid of proper working curves and tables, to calculate the heterogeneous rate constant. Even if this method is simple and widely used it must be pointed out that in some cases uncompensated resistance can give effects on peak separation that are similar to those due to kinetic limitations of the system. The effect of uncompensated resistance is particularly critical when the current is large and when \( k_0 \) approaches the reversible limit, so that \( \Delta E_p \) differs only slightly from the reversible value.

### 3.1.4 Differential pulse voltammetry

Differential pulse voltammetry is mainly used to reach better sensitivities than potential sweep and normal pulse techniques. The main advantage of DPV is the large

supression of the non faradic current. Figure 45 depicts the potential program usually employed for differential pulse experiments.

![Potential program for a differential pulse polarographic experiment.](image)

The figure refers to a specific case of differential pulse polarography, but the waveform and the measurement strategy are general for the method in its broader sense. It is applicable to every solid state electrode. The base potential is changed steadily in small increments to a final value. Potential pulses of small height (10-100 mV) are superimposed to the base potential. Two current samples are taken during each pulse lifetime, one at $\tau'$ immediately before the pulse and the second at $\tau$ late in the pulse, just before it ends. The record of the experiment is a plot of the current difference ($\delta i = i(\tau) - i(\tau')$) versus the base potential. The differential measurement gives a peaked output (Figure 46). The reason is easily understood qualitatively: when the base potential is too small to activate the electron transfer no faradic current flows before the pulse and the change in potential manifested in the pulse is too small to stimulate the faradic process, thus $\delta i = i(\tau) - i(\tau')$ is virtually 0, at least for the faradic component. Late in the experiment when the base potential is in the diffusion-limited-current region the electroactive specie reacts at the maximum rate possible and the pulse cannot increase the current further; hence $\delta i$ is again small. Only in the region near $E^0$ there is an appreciable faradic current observed, in fact only in potential regions where a small potential difference can make a sizeable difference in current flow does the differential pulse technique show a response.
For a reversible case it can be shown\textsuperscript{79} that:

$$E_{\text{MAX}} = E_{1/2} - \Delta E / 2$$  \hspace{1cm} (3.6)

Where $E_{\text{MAX}}$ is the peak potential and $\Delta E$ is the pulse height. Since $\Delta E$ is small, the potential of maximum current lies close to $E_{1/2}$.

\section*{3.2 Solar Cell Assembly}

\subsection*{3.2.1 Mesoporous oxide paste preparation.}

The colloidal TiO$_2$ paste involves the controlled hydrolysis of Ti(IV) isopropoxide followed by peptization in acidic water to produce a sol, a colloidal liquid. Autoclaving these sols (heating at 200-250 °C for 12 h) allows the controlled growth of the primary particles and improves their crystallinity. During the hydrothermal growth smaller particles dissolve and fuse together to form larger particles by a process known as Ostwald ripening. The resulting TiO$_2$ particles consist of Anatase or of a mixture of Anatase and Rutile. The Sol-Gel process is ideal for the preparation of mesoporous semiconductor oxides: it is simple and

requires common laboratory instrumentations, the starting materials are not needed at a particularly high purity level and are commonly available at low cost.

A typical preparation involves the slow addition of 50 ml of Ti(IV) Tetraisopropoxide to 300 ml of deionized water acidified with 2.1 ml of concentrated HNO₃. The formation of a white TiO₂ precipitate is immediately observed. The resulting mixture is heated at 80 °C for 8 hours during which the peptization of the precipitate and the formation of a colloidal suspension occurs. The suspension is allowed to concentrate to about 100 ml corresponding to a TiO₂ concentration of about 150 g/l. The average diameter of colloidal nanoparticles is estimated to be 5-8 nm. The colloidal sol is autoclaved at 220 °C for 12 h. During this process the hydrothermal growth of the nanoparticles occurs and a white colloidal paste is obtained. 3-3.5 g of Carbowax, a polymer that acts both as a tensioactive and as a binder, are then added to the paste and the mixture is stirred at room temperature for 6-8 hours, after that the colloid is ready for deposition on the TCO substrate.

3.2.2 Photoanodes preparation.

The transparent conductive oxide (TCO) of choice for realizing DSSCs is an highly fluorine doped SnO₂ film (FTO-Fluorine-Tin-Oxide) deposited on glass. The average surface conductivity of the conductive glasses used in this work is about 10 Ω/sq. SnO₂:F allows an effective light transmission while providing good conductivity for current collection, in addition it establishes a good mechanical and electrical contact with the dye sensitized oxide in order to obtain a satisfactory electronic percolation from the semiconductor to the electron collector. The conductive glass is covered on two parallel edges with 3M adhesive tape (ca 20 μ thick) to control the thickness of the TiO₂ film. The colloid is applied to one edge of the conducting glass and distributed with a glass rod sliding over the tape-covered edges. After air drying, the electrodes are heated in an oven at 450°C for 30 min in the presence of air. The resulting film thickness is of the order of 6-7 μm. A solution c.a 10⁻⁴ M of a proper sensitizer dissolved in an appropriate solvent is used to carry out sensitization of the photoanodes. Usually the dye adsorption is conducted at reflux for 3-5 hours. Experimental details about the dye adsorption conditions are reported in Chapters 4, 5 and 6.
3.2.3 Counter electrodes.

Different kinds of counter electrodes were used: platinum coated counter electrodes, gold coated electrodes and carbon coated electrodes. Platinum metal clusters were deposited on FTO electrodes by spraying a $5 \times 10^{-3}$ M solution of hexachloroplatinic acid in isopropanol. The procedure is repeated 5-7 times until an homogeneous distribution of hexachloroplatinic acid clusters on the surface is observed. The resulting surfaces are then dried in air for 5 minutes and cured at 380°C in an oven for 15 minutes, during which the pyrolysis of the hexachloroplatinic acid occurs and metallic Pt clusters are formed. This procedure creates transparent counter electrodes. Reflective Pt coated glasses were obtained by Pt sputtering. Gold covered electrodes were obtained by thermal evaporation. Usually, due to the poor stability of the Au deposit on FTO, a chromium underlayer few nanometers thick was previously deposited by thermal evaporation or controlled electrolysis on the conductive glasses, and subsequently the deposition of a gold layer 20-30 nm thick on chromium was performed. Carbon coated electrodes were obtained by spraying the surfaces 5–6 times with Areodag G (Achelson) graphite spray. The carbon deposit produced in this way was very fragile, and fragmentation of the coated surface was commonly observed after a single use of this kind of counter electrode.

3.2.4 Cell Assembly.

Two kinds of cells were prepared: open cells and closed cells. Open cells are made by simply pressing together the photoanode and the counter electrode and blocking the glasses together with small metal clamps. The electrolyte was allowed to fill the gap between the sensitized semiconductor and the counter electrode by capillarity. In many cases a suitable parafilm® spacer inserted between the electrodes allows to confine the electrolytic solution inside the cell for longer times, leading to a more stable cell configuration required for prolonged experiments. This kind of cells are also called “thick” cells because there is a thicker layer of electrolyte between the photoanode and the cathode. Closed cells are cells sealed by melting a thermoplastic polymer (Surlyn®, 400 nm thick) inserted between the
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anode and the counter electrode that, on cooling, firmly binds the two electrodes to each other. The electrolyte was injected through a small hole with a pump that created vacuum in the cell. The hole was then sealed with ephoxy resin. The closed cell configuration is required for stability tests of DSSCs when it is necessary to confine the electrolytic solution inside the cell for very long periods, even months. Solar cells without spacer are built by directly pressing the TiO₂ photoanode over the counterelectrode; the mediator solution is later introduced by capillarity inside the cell, obtaining a liquid layer of substantially reduced thickness compared to the previous case. This cell configuration is less stable than the former. In both cases metallic clamps are used to hold firmly the two electrodes together.

The electrolyte preparation will be described in detail in Chapter 4.

3.3 DSSCs Characterization

The performance of the cell can be quantified on a macroscopic level with parameters such as Incident Photon to Current Efficiency (IPCE), open circuit photovoltage ($V_{oc}$), and the overall efficiency of the photovoltaic cell, $\eta_{cell}$.

The parameter that directly measures how efficiently incident photons are converted to electrons is the IPCE. The wavelength dependent IPCE term can be expressed as a product of the quantum yield for charge injection ($\Phi$), the efficiency of collecting electrons in the external circuit ($\eta$) and the fraction of radiant power absorbed by the material or light harvesting efficiency (LHE), as represented by Equation 3.7:
IPCE = (Φ_{inj})(η)(LHE) \tag{3.7}

While Φ and η can be rationalized on the basis of kinetic parameters, LHE depends on the active surface area of the semiconductor and the cross section for light absorption of the molecular sensitizer. In practice the IPCE measurements are performed with monochromatic light and IPCE(λ) values are calculated according to Equation 3.8.

$$\text{IPCE}_\lambda = 1.24 \times 10^3 \text{(eV nm)} \cdot \text{I}_\text{sc} (\mu\text{A cm}^{-2}) / \lambda (\text{nm}) \cdot I (\text{mW cm}^{-2})$$ \tag{3.8}

In Equation 3.8, I_{sc} is the photocurrent density produced by the cell, λ the excitation wavelength and I the incident photon flux.

The light harvesting efficiency, or absorption factor, is related to the dye molar extinction coefficient (ε(λ), L·mol^{-1}·cm^{-1}) and to the surface coverage (Γ, mol·cm^{-2}) by Equation 3.9.

$$\text{LHE}_\lambda = 1 - 10^{-[1000ε(λ)Γ]}$$ \tag{3.9}

An absorption factor above unity is ideal for a solar energy device as almost all the incident radiant power is collected.

In the absence of photodecomposition reactions, the quantum yield for electron injection from the excited sensitizer to the semiconductor is given by Equation 3.10.

$$\phi_{\text{inj}} = \frac{k_{\text{inj}}}{\sum k_d + k_{\text{inj}}}$$ \tag{3.10}

where k_{inj} is the rate constant for electron injection and Σ k_d is the sum of all rate constants for the excited state deactivation processes. Charge injection from the excited dye will be activated if the donor energy is positive with respect to the conduction band edge (E_{CB}). Electron injection will be, on the contrary, activationless if the donor level has energy equal to or more negative than the conduction band edge. This condition is met when E(S+/S^*) + λ > E_{cb}, where E(S+/S^*) represents the excited state oxidation potential of the sensitizer.
(which is related to the ground state oxidation potential and to the spectroscopic energy by:
\[ E_{(S+/S^-)} = E_{(S+/S^0)} - E_{oo} \] and \( \lambda \) represents the reorganization energy accompanying the charge injection process.

The fraction of injected charges which percolate through the TiO\(_2\) membrane and reach the back contact of the photoanode is represented by the factor \( \eta \). It has been shown that the electron diffusion length (\( L_n \)), which is a key parameter for charge collection, given by
\[ L_n = \sqrt{D_0 \tau_0} \] (\( D_0 \) and \( \tau_0 \) are the diffusion coefficient and lifetime of electrons in conduction bands), is of the order of 20-100 \( \mu m \) for the liquid electrolyte based DSSCs, allowing thus to use relatively thick photoanodes for optimizing the light harvesting efficiency of the solar device. It is accepted that electron diffusion occurs with an ambipolar mechanism, which involves simultaneous motion of electrons and electrolyte cations. Although the diffusion coefficient of cations in the nanoporous network are normally small, high concentrations of cations, intercalated between the semiconductor nanoparticles, support a fast transport of the electrons as minority carriers, as shown by electron-density-dependent diffusion coefficients when high-ion-concentration electrolytes are used.

Moreover J-V curves under white light are useful to determine the quality of the cell as source of power and necessary to determine the global photovoltaic performance of the system. The general current-voltage characteristic of a solar cell may be approximated by the diode equation\(^\text{80}\):
\[
I = I_{ph} - I_S\left(\frac{V_{oc}}{V_{oc}} - 1\right) - \frac{V_a}{R_{sh}}
\] (3.11)

Where \( I \) is the current, \( I_S \) is the saturation current of the diode, \( I_{ph} \) is the photocurrent which is assumed to be independent by the applied voltage \( V_a \). \( R_{sh} \) is the shunt resistance of the circuit and is introduced to take into account the internal resistance and energy dissipation mechanisms of the cell.

\( V_t \) is the thermal voltage given by \( V_t = \frac{n k T}{e} \).

Equation 3.11 can be obtained from the circuit represented in figure 48 which shows the equivalent circuit of the cell. Obviously it is only a simplified model of the DSSC which is

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actually thought to correspond to a multi-diode model to take into account the different mechanisms of charge transport within the cell.

![Diode Model Diagram]

**Figure 48.** The DSSC under irradiation can be expressed as a non-perfect current generator mounted in parallel to a non-perfect diode.

Figure 49 shows a typical i-V response of a solar cell with the power curve in the lower part. There will be a couple of current and voltage values whose product gives the maximum power output of the cell. The dots represent the maximum power output.

![i-V Curve Diagram]

**Figure 49** i-V curve showing the variations in photocurrent and power as a function of the potential.

The short circuit current $I_{sc}$ is the cell photocurrent measured at zero voltage, when the series resistance $R_s$ is minimal. Therefore $V_s = 0$ and $I_{sc} = I_{ph}$. $J_{sc}$ is simply the short circuit current divided by the active area of the cell. The open circuit photovoltage $V_{OC}$ is the cell potential measured when the current within the cell is equal to zero. $V_{OC}$ can be obtained from (3.11) by setting $I = 0$ and $V_s = V_{OC}$. Under these conditions:
\[ V_{OC} \approx V_i \ln \left( \frac{I_{ph}}{I_S} \right) \]  

(3.12)

Obvioulsy both \(I_{sc}\) and \(V_{OC}\) are functions, through \(I_{ph}\), of the irradiance.

Experimentally \(i-V\) curves are collected by imposition of an external potential in opposition to the cell, sweeping it from zero to the \(V_{OC}\) value of the cell under illumination, and recording the current as a function of the external potential. When the applied potential is zero, the cell is in short circuit conditions, while when the external potential matches the open circuit potential the current drops to zero.

The fill factor (FF) measures the cell’s quality as a power source and is therefore the ratio between the maximum power and the external short circuit current and open circuit voltage.

\[
FF = \frac{I_M V_M}{I_{SC} V_{OC}}
\]

(3.13)

This parameter indicates the deflection of the curve from a square like curve, and is always minor than unity.

The efficiency \(\eta\) describes the performance of the solar cell and is defined as the ratio of the maximum electric power generated by the cell to the incident radiation power on the solar cell surface:

\[
\eta = \frac{I_{SC} V_{OC} FF}{P_{in}}
\]

(3.14)

As the efficiency is a function of \(I_{SC}, V_{OC}\) and FF, improvement of the photovoltaic yield is achieved by optimization of these three parameters.

### 3.4 Laser Flash Photolysis

Electron transfer dynamics at the Semiconductor/Dye/electrolyte interface were studied mainly by time resolved absorbance measurement. Following the excitation pulse, a population of excited dye molecules able to inject charge into the semiconductor is created. The electron injection is much faster (fs-ps) than the time resolution of the technique employed (ns), so that a population of oxidized dye molecules is instantaneously created. The
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decay of the oxidized dye absorption recorded in various conditions gives information about the efficiency of charge transfer from the electron mediator and about the dynamics of electron recapture. Laser Flash Photolysis (LFP) was also used to determine the excited state lifetime in solution of several sensitizers studied in this thesis work.

3.4.1 Experimental apparatus.

The transient absorption apparatus is schematized in figure 50:


The excitation source is a solid state Nd-Yag laser equipped with Q-switch and frequency multipliers in order to obtain 532, 355 and 266 nm excitation wavelengths with a pulse amplitude at half width of about 7 ns. A continuous 150 Xe lamp generates the analysis light which is oriented at 90° with respect to the excitation beam. A computer controlled external trigger synchronizes all the components of the apparatus. Time resolved absorption studies were carried out using the 532 nm excitation, attenuating the pulse energy by means of a KMnO₄ filter to the value of 0.25 mJ/pulse. The sample, a solid sensitized TiO₂ film sintered on a microscope slide was oriented at 45° with respect to the excitation pulse. An interferential filter placed in front of the monochromator provided the elimination of the intense 532 nm light scattering. The oxidized dye recovery was observed at different wavelengths according to the different sensitizer specie. Satisfactory signal to noise ratio
were usually obtained by averaging 20/30 shots. In these conditions the transient absorption decays approached quite satisfactory a mono-exponential behaviour, in particular in presence of electron mediators. At higher pulse intensities a multiexponential behaviour gradually appeared, probably due to an increase in recombination rate determined by a larger electronic concentration in the semiconductor and by intraband states population.

3.4.2 Transient Absorption.

Before the laser pulse (time zero) only dye molecules at the ground state, whose concentration and extinction coefficient are respectively $[A_0]$ and $\varepsilon_A$, are present in the sample. After excitation a population of oxidized dye is created, with a certain concentration $[A]^+_t$ and extinction coefficient $\varepsilon_A^+$. For these reasons the absorption of the analysis light at a particular wavelength $\lambda$ will be different before and after the laser pulse. The laser induced absorption variation is subjected to a temporal evolution according to the time evolution of oxidized sensitizer population. The oscilloscope detects a time dependent tension which is proportional to the light intensity transmitted through the sample.

Before the excitation the optical density of the sample is given by:

$$\log \frac{I_0}{I_t} = \varepsilon_A [A_0] l = OD$$

(3.15)

where $I_0$ and $I_t$ are the light intensities transmitted at time 0 and $t$ and $l$ is optical path.

After excitation:

$$\log \frac{I_0}{I_t^+} = \varepsilon_A [A] l + \varepsilon_A^+ [A]^+_t l = OD^+$$

(3.16)

where $[A]_t = [A]_0 - [A]^+_t$

The resulting difference in optical density, detected by the oscilloscope will be given by:

$$\Delta OD = \log \frac{I_0}{I_t^+} - \log \frac{I_0}{I_t} = (\varepsilon_A^+ - \varepsilon_A)[A]^+_t$$

(3.17)

Usually the absorption coefficient of the oxidized dye (Ru(III)) is smaller than the absorption coefficient of Ru(II) (at least in large part of the visible region) thus $\Delta OD$ assumes negative values (bleaching). The considerations reported here are obviously of general validity and can be extended to every case in which the generation and the evolution of a
population of chemical species with different absorption properties with respect to their initial state is monitored spectroscopically. In many cases the excited state absorption can be stronger than the ground state, in this case $\Delta\text{OD}$ will be positive.

### 3.4.3 Transient Emission.

The same apparatus depicted in figure 50 also works for collecting transient emission. Obviously the lamp and the other equipment for absorption is not necessary and not used. Emission from the excited sample is collected at 90°. Assuming an instantaneous formation of the excited state, the laser flash produces a concentration of an excited chemical specie $[A]_0^*$ which deactivates by emitting radiation of certain frequencies. The intensity of emitted light is proportional to the excited state concentration. In the simplest case the emission of radiation is described by a first order process.

$$A^* \rightarrow A + h\nu$$

$$-\frac{d[A]^*}{dt} = \frac{1}{\tau} [A]^*$$

Whose integration gives

$$[A]^* = [A]_0^* \exp(-t/\tau)$$

Also

$$I(\lambda) = I_0(\lambda)e^{-t/\tau}$$

Thus the emission profile is mono-exponential and its time constant, obtained by linearization of (3.20) or direct fitting of the decay gives directly the lifetime of the excited specie.