

## The application of diffuse reflectance laser photolysis to study photochemistry at interfaces and in dyed fabrics

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**Abstract.** Recently we have extended to heterogeneous, opaque and often highly scattering systems, the application of flash photolysis by using diffuse reflected light instead of transmitted light as the analysing source on timescales extending from several seconds to picoseconds. Laser-induced transient spectra and decay kinetics have been observed from a wide variety of samples including fractions of monolayers of organic molecules adsorbed on catalytic metal oxide surfaces, within inorganic and organic microcrystals, from dyed fabrics and from paper pulp. The potential of the technique to study photochemical reactions at interfaces is demonstrated with particular reference to ion-electron recombination on porous silica surfaces and to photochemical and photophysical processes occurring in dyed fabrics.

**Keywords.** Diffuse reflectance; laser photolysis; photochemistry; reaction at interfaces; reaction in dyed fabric.

### 1. Introduction

The technique of flash photolysis has been extensively applied to study rapid homogeneous reactions in the gas phase and in dilute fluid and rigid solutions (Porter and West 1974). Kessler and Wilkinson (1981) demonstrated that the technique can be extended to opaque samples by monitoring changes in the diffuse reflected light from an analysing source following pulsed photo-excitation. In 1984 we reported the first successful diffuse reflectance pulsed radiolysis experiments (Wilkinson *et al* 1984) and more recently (Wilkinson *et al* 1986a) we have demonstrated that diffuse reflectance picosecond laser flash photolysis studies are possible using mode-locked picosecond lasers and pump-probe methods. Photoinduced transient spectra and decay kinetics have already been observed from a wide variety of opaque samples including fractions of monolayers of organic molecules adsorbed on catalytic metal oxide surfaces (Oelkrug *et al* 1988, 1989) and included within zeolites (Kelly *et al* 1990), from semiconductor powders (Wilkinson *et al* 1986b) and doped and undoped porous electrodes (Kossanyi *et al* 1990), from ruthenium(II) complexes within ion exchange resins (Masschelein *et al* 1991), from organic microcrystals (Wilkinson and Willsher 1984), and from organic dyes adsorbed on microcrystalline cellulose (Wilkinson *et al* 1991b, 1992), on fabrics and chemically bound to polymers

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(Bourdelaude *et al* 1988; Wilkinson *et al* 1990), from paper pulp (Schmidt *et al* 1990) and from photographic emulsions (Wilkinson and Leicester, to be published). Other groups are now increasingly using this method to study the mechanisms of light-induced reactions in heterogeneous environments (Turro *et al* 1986; Ikeda *et al* 1988; Draper and Fox 1990; Levin *et al* 1990).

## 2. Experimental

The equipment used for laser flash photolysis in diffuse reflectance mode is identical to that used for studies in transmission mode except for the geometry for collecting the analysing light which is diffusely reflected from the excited sample. Full experimental details and more extensive discussions of the analysis of data are given elsewhere (Wilkinson 1986; Oelkrug *et al* 1987). Following the Kubelka–Munk treatment (Kubelka 1948) for diffuse reflectance, two light fluxes are considered travelling in opposite directions perpendicular to the irradiated surface at  $x = 0$ . The attenuation of the incident flux  $I$  depends on the absorption and scattering coefficients  $K$  and  $S$  respectively and is given by:

$$dI(x) = -I(x)(K + S)dx + J(x)Sdx, \quad (1)$$

and the generated flux, since it passes in the opposite direction, has:

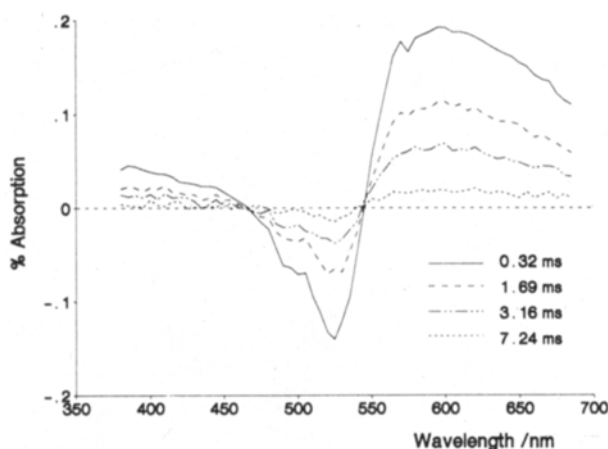
$$dJ(x) = J(x)(K + S)dx - I(x)Sdx. \quad (2)$$

The diffuse reflectance  $R$  is given by  $R = J_0/I_0$ , where  $I_0$  and  $J_0$  are the incident and reflected fluxes at the surface. Equations (1) and (2) can be solved for a layer so thick that any further increase in thickness does not affect  $R$  and provided  $K$  and  $S$  are independent of  $x$  this gives:

$$(1 - R)^2/2R = K/S = F(R). \quad (3)$$

The remission function,  $F(R)$ , is linearly dependent on the number of absorbing chromophores in any sample when  $S$  and  $K$  are independent of the penetration depth below the surface.

In diffuse reflectance flash photolysis the initially excited chromophores are usually homogeneously distributed. However, photo-excitation produces transient or permanent changes in absorption, preferentially just below the irradiated surface. Theoretical treatments show that there are two limiting types of concentration profile produced, namely an exponential fall-off as a function of penetration depth and a homogeneous (or “plug”) profile. The latter case is encountered with large laser fluencies and with low concentrations of ground state absorbers, where there is total conversion from ground state to transient to a certain depth below the irradiated surface. Since a homogeneous concentration of absorbers exists, the Kubelka–Munk theory can be applied. For optically thick samples at analysing wavelengths where only the transient absorbs, the remission function given by (3) is a linear function of the concentration and can be used for kinetic analysis and for plotting absorption spectra. For low percentage conversions the concentration of transients decreases exponentially below the irradiated surface. An analytical solution for the change in



**Figure 1.** Time-resolved transient difference spectra obtained following diffuse reflectance laser flash photolysis of eosin adsorbed on cotton fabric.

reflectance expected has been obtained by Lin and Kan (1970) and is in the form of a converging series.  $\Delta R$ , the observable in-diffuse reflectance laser flash photolysis is defined as follows:

$$\Delta R(t) = [R_b - R(t)]/R_b, \quad (4)$$

where  $R_b$  and  $R(t)$  are the reflectance before and at time  $t$  after exposure to laser excitation. For low percentage conversions, the parameter  $\Delta R$  has been shown to be a linear function of concentration of the transient provided  $\Delta R < 0.1$  (Oelkrug *et al* 1987). Often  $100 \Delta R$  is referred to as the percentage absorption by the laser induced transient. Full experimental details are given elsewhere (Wilkinson and Kelly 1990).

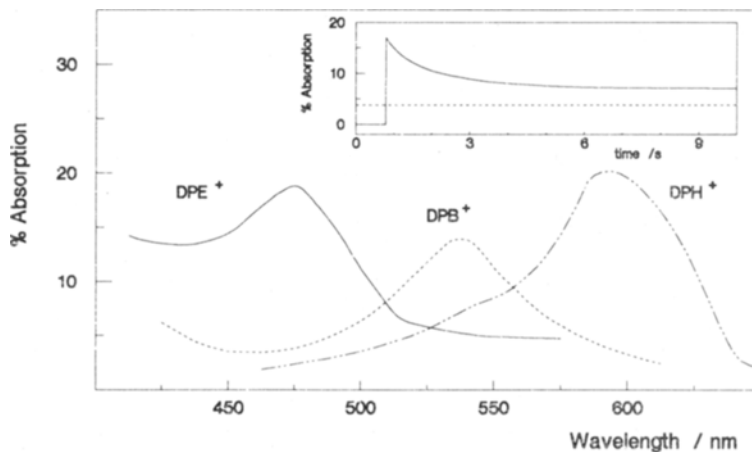
As in all flash-photolysis experiments one obtains transient difference spectra and decreases in absorption are often observed at wavelengths where the ground state has a stronger absorption coefficient than the transient. Figure 1 gives an example, which shows excellent isosbestic points, obtained by laser excitation at 532 nm of eosin adsorbed on cotton fabric.

If the absorption coefficient  $K$  is in excess of  $10^4 \text{ cm}^{-1}$  at the laser excitation wavelength, then the penetration depth is only about  $1 \mu\text{m}$  and dissipation of laser excitation as heat causes considerable temperature rises (Wilkinson *et al* 1986b). This possibility has always to be borne in mind and lower laser fluences, lower concentrations or excitation into weaker bands must be employed to avoid thermal effects on some samples.

### 3. Results and discussion

#### 3.1 Radical cation–electron recombination

Adsorbed radical cations have been detected by the method of diffuse reflectance laser flash photolysis using polycrystalline microporous catalytic metal oxides such as silica and alumina as adsorbents (Oelkrug *et al* 1988). We have studied several diphenylpolyenes adsorbed on alumina. Typical transient absorption spectra obtained



**Figure 2.** Transient absorption spectra from radical cations on alumina (DPE, DPB and DPH represent diphenyl-ethene,-butadiene and -hexatriene, respectively).

for 1,2-diphenylethene (DPE), 1,4-diphenylbutadiene (DPB) and 1,6-diphenyl-1,3,5-hexatriene (DPH) adsorbed on alumina recorded 1 ms after excitation are shown in figure 2. These transients are long-lived and decay non-exponentially with the first half-life considerably shorter than the second half-life and so on. In the case of DPH on alumina, we also observed (Oelkrug *et al* 1988) a much shorter-lived transient which we have assigned to the adsorbed triplet state of DPH. There is strong evidence that the long-lived transients in DPE, DPB and DPH are radical cations. Thus for DPE adsorbed on  $\text{Al}_2\text{O}_3/\text{SiO}_2$  the radical cation is known to have its stronger absorption band at 480 nm, while for DPB and DPH adsorbed on this catalyst the strongest ground-state absorption bands of the radical cations occur at 542 and 602 nm respectively (Kortu and Schlichenmaier 1966). In solution a short-lived transient ( $\tau < 100$  ns,  $\lambda_{\text{max}} = 478$  nm) is reported after flashing charge-transfer complexes of DPE in the presence of an electron-acceptor such as fumaronitrile (Goodman and Peters 1985). This transient is assigned as the radical cation. We have proved this assignment by measuring the ESR spectra of these adsorbed radical cations at low temperatures (Oelkrug *et al* 1991).

From studies of the dependence of the amounts of radical produced as a function of laser intensity coupled with the computer modelling of the transient concentration profile it is possible to show that the production of the radical cation is a multiphoton process (Oelkrug *et al* 1991) probably involving the consecutive absorption of two photons.

The decay of these transients has been shown to be very dependent on the temperature, on the nature of the adsorbent and on its pre-treatment. Repetitive excitation at room temperature of the same sample area at intervals of a few minutes demonstrates that the intensity of absorption and the decay kinetics of the radical cation are reproducible. Thus the radical cations decay almost exclusively to give back that original molecule. Thus the complex decay is due to radical cation-electron recombination. Variation in surface coverage of adsorbates gives only very small difference in the kinetics observed. This suggests that the process of ionization leaves the radical cation and the electron separated by a small distance (smaller than the nearest distance between adsorbates) and that geminate pair recombination is the

decay mechanism. The decays fit quite well the expression,

$$C_0/C = 1 + \alpha t^{\frac{1}{2}},$$

where  $C_0$  and  $C$  represent the concentrations of the radical cations formed initially and remaining after time  $t$ . The values of  $\alpha$  are strongly dependent on temperature, adsorbent and on the adsorbate (Oelkrug *et al* 1991).

### 3.2 Triplet-triplet energy transfer

Triplet-triplet energy transfer has been studied between benzophenone and an oxazine dye (2,7-bis(diethyl-amino)-phenazonium chloride) co-adsorbed on the surface of microcrystalline cellulose (Wilkinson *et al* 1991b). Ground-state absorption and fluorescence measurements provide evidence for dimer formation of the oxazine dye when adsorbed on cellulose, in contrast to the behaviour in ethanol solution where no dimerisation occurs. The efficiency of energy transfer from triplet benzophenone was studied using both time-resolved absorption and phosphorescence intensity measurements, lifetime measurements indicating that the energy transfer process involves static quenching.

From the sensitised transient difference spectrum (figure 3) of the oxazine dye it has been possible to evaluate the triplet state extinction coefficient relative to that of triplet benzophenone. The ratio of extinction coefficients is found to be identical to that determined in acetonitrile solution (Wilkinson *et al* 1991a).

### 3.3 Dyed fabrics

It is very important to be able to understand the photochemical and photophysical behaviour of the compounds employed to colour natural and synthetic fibres, especially from a commercial point of view. Although it has been possible to obtain useful information from ground state reflectance spectroscopy and luminescence studies of a dyed fabric, a flash photolysis investigation of the photophysical properties has not been possible hitherto. It was thus necessary to undertake model studies of the dye in solution, simply because transmission flash photolysis cannot be applied to a piece of cloth. The data obtained from model studies had then to be extrapolated

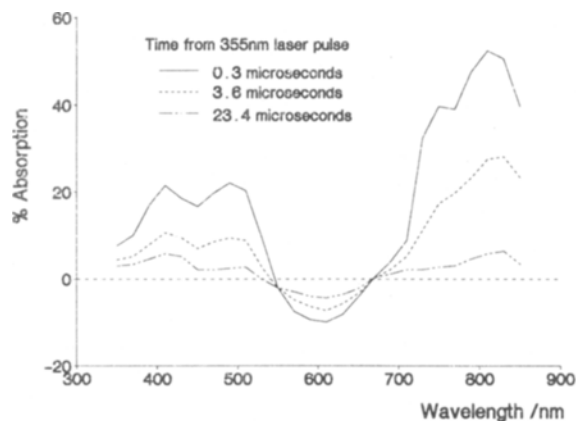


Figure 3. Time-resolved transient difference spectra from  $1.8 \times 10^{-4} \text{ mol g}^{-1}$  of benzophenone and  $2 \times 10^{-5} \text{ mol g}^{-1}$  of oxazine coadsorbed on microcrystalline cellulose.

to the environment of a woven fabric, which is quite different from a fluid solution. It is clearly more satisfactory to be able to apply flash photolysis directly to a dyed fabric, and this is now possible using diffuse reflectance laser photolysis. In this section, some results obtained from cotton fabric dyed with phthalocyanine and fluorescein derivatives will be discussed.

**3.3a Cotton fabric dyed with sulphonated aluminium(II) phthalocyanine:** Non-fluorescent woven cotton fabric dyed with sulphonated aluminium phthalocyanine shows both transient absorption and ground state depletion following excitation at 354 nm (intensity = 15 mJ per pulse) (Wilkinson and Willsher 1985). The spectral band observed with  $\lambda_{\text{max}}$  around 500 nm indicated that the transient absorption arose from the lowest triplet state. In addition, ground-state depletion is observed around 650 nm. The decay of the absorption follows a first-order rate law in a water-free fabric with  $\tau \sim 0.75$  ms, in the presence or absence of oxygen. Quenching by oxygen occurs only if the fabric is water saturated, and even then the overall quenching process is inefficient, since the decay of the absorption cannot be fitted as a pseudo-first-order process. A similar effect is observed if other potential quenchers are present in the fabric. It must be concluded that the rate of diffusion of molecules through the fibres is very much slower than in solution; this is an important factor in determining the rate of reactions which may occur in the fabric between the dye and other molecules such as fluorescent brightening agents or detergents.

**3.3b Cotton fabric dyed with halogenated fluorescein dyes:** The triplet-triplet ( $T-T$ ) absorption of halogenated fluorescein dyes (eosin, erythrosin and rose bengal) contained in cotton fabric can be readily detected following excitation at either 354 or 532 nm. Figure 1 shows the transient difference spectrum for eosin on non-fluorescent cotton cloth. The positive part of the spectrum from 550 to 680 nm corresponds to absorption from the first triplet state of the dye, while the negative portion represents depletion of the ground state. The decay of the  $T-T$  absorption follows a mixed first- and second-order process. Similar spectral and kinetic behaviour is found for rose bengal (Wilkinson *et al* 1985) and erythrosin dyed into cotton. As in the case of sulphonated aluminium phthalocyanine on cotton, water is necessary to observe partial quenching by oxygen of the triplet state of the fluorescein dyes. In the laser-induced emission spectrum of rose bengal in cotton fabric phosphorescence of the dye at 765 nm can be observed since this has the same decay parameters as the  $T-T$  absorption (Wilkinson *et al* 1985). A smaller feature at 650 nm disappears more rapidly than the phosphorescence, and occurs at wavelengths where fluorescence from rose bengal would be expected. Its lifetime is too long for this feature to be prompt fluorescence, and it is more likely to be delayed fluorescence which results from  $T-T$  annihilation. This process would account for the fact that the early part of the  $T-T$  absorption decay is dominated by a second-order process. It is interesting to note that for rose bengal adsorbed onto different substrates the relative sizes of the emission signals at 650 and 765 nm vary. When adsorbed on nylon or polyacrylamide the emission spectrum is similar to that on cotton fabric but the majority of the decay of the  $T-T$  absorption obeys a first-order rate law. With polystyrene as the substrate the delayed fluorescence at 650 nm predominates and virtually no phosphorescence is detected. For this sample the  $T-T$  absorption is much shorter lived and decays almost entirely by a second-order rate law. It seems that polystyrene

is a substrate which allows intermolecular  $T-T$  energy transfer to take place more readily than the other adsorbents.

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