

## Diffuse reflectance laser flash photolysis of adsorbed molecules

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**Abstract.** Recent progress which allows laser flash photolysis investigation of opaque materials by using diffuse reflectance from analysing sources for the detection of laser induced transient species is described. Experimental details of nanosecond and picosecond diffuse reflectance laser photolysis systems are presented and methods of analysis of data are discussed. The potential of the technique for studying elementary reactions at interfaces is demonstrated with particular reference to bimolecular reactions of (a) the triplet state of acridine adsorbed on various porous silica surfaces and (b) ion-electron recombination following multi-photon ionisation of diphenyl polyenes adsorbed on  $\gamma$ -alumina. The mechanisms of formation and decay of these transient adsorbed species are discussed.

**Keywords.** Adsorbed molecules; laser photolysis; kinetics; transient spectra.

### 1. Introduction

Flash photolysis, first developed by Porter (1950), is a most powerful technique which has been extensively applied to study rapid homogeneous reactions in the gas phase and in dilute fluid and rigid solutions. 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. Wilkinson *et al* (1984) reported the first successful diffuse reflectance pulsed radiolysis experiments and more recently have demonstrated that diffuse reflectance picosecond laser flash photolysis studies are possible using mode locked picosecond laser and pump-probe methods (Wilkinson *et al* 1986b). Ikeda *et al* (1987) have already followed up this advance and obtained photoinduced time resolved spectra in the picosecond time domain.

Laser induced transient spectra and decay kinetics have been observed in our laboratory from a wide variety of samples including fractions of monolayers of organic molecules adsorbed on catalytic metal oxide surfaces (Oelkrug *et al* 1988, 1989) and included within the hydrophobic man-made zeolite silicalite (Wilkinson *et al* 1986a) from semiconductor powders (Wilkinson *et al* 1986c) and sintered porous electrodes doped and undoped (Pouliquen *et al* 1986; Kossanyi *et al* 1990) from organic and inorganic microcrystals (Wilkinson and Willsher 1984, 1988) and from dyes adsorbed on fabrics and chemically bound to polymers (Wilkinson and Willsher 1985; Wilkinson *et al* 1987). For recent reviews see Wilkinson (1986), Wilkinson and Kelly (1990) and Wilkinson and Willsher (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 used for collecting the analysing light (see figure 1) 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 2 gives an example, which shows excellent isosbestic points, obtained by laser excitation at 532 nm of eosin adsorbed on microcrystalline cellulose. This spectrum, although much broader, bears a close resemblance to the solution triplet spectrum (Kasche and Lindqvist 1985). Analysis of transient changes in diffuse reflectance can follow the Kubelka–Munk treatment (Kubelka 1948) where two light fluxes  $I$  and  $J$  are considered to be travelling in opposite directions perpendicular to the irradiated surface at  $x = 0$ . These fluxes depend on the absorption and scattering coefficients  $K$  and  $S$  respectively, with the attenuation of the incident flux given by

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

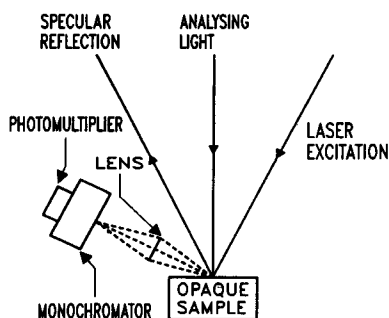


Figure 1. Schematic diagram of the sample geometry used in diffuse reflectance laser flash photolysis.

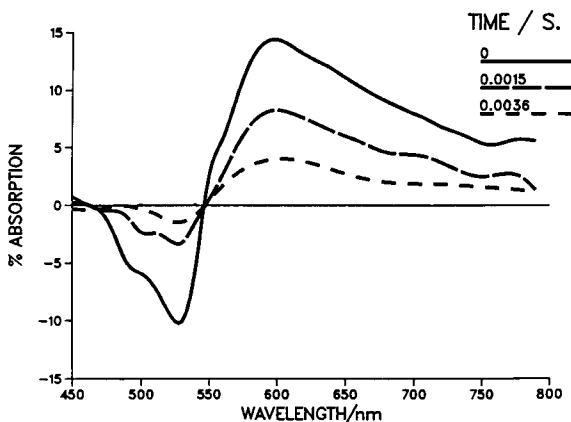


Figure 2. Time resolved transient difference spectra obtained following diffuse reflectance laser flash photolysis of eosin adsorbed on microcrystalline cellulose.

The generated flux  $J$  since it is moving in the opposite direction has the opposite sign i.e.

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

The diffuse reflectance  $R = J_0/I_0$ , where  $I_0$  and  $J_0$  are surface incident and reflected fluxes. 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

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

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

In diffuse reflectance flash photolysis the ground state chromophores, which are excited, are usually homogeneously distributed. However, photo-excitation gives 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 fluences 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 the low percentage conversions the concentration of transients decreases exponentially below the irradiated surface. Under these conditions  $(1 - R_t^a)$ , where  $R_t^a$  is the relative transient reflectance at the analysing wavelength, is a linear function of the concentration of the transient species at values of  $(1 - R_t^a)$  less than 0.1 (Oelkrug *et al* 1987).

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  $\sim 1 \mu\text{J}$  and dissipation of laser excitation as heat causes considerable temperature rises (Wilkinson *et al* 1986c). This possibility has always to be borne in mind, and lower laser fluences and/or lower concentrations and/or excitation into weaker bands must be employed to avoid thermal effects for some samples.

### 2.1 Picosecond diffuse reflectance laser photolysis

Figure 3 illustrates the basic arrangement used to record the first ever transient absorption within an opaque material on picosecond timescales using diffuse reflectance. Generation and detection of the transient absorption was effected by pumping the sample at 295 nm (pulse width = 6 ps, energy =  $20 \mu\text{J}$ ) and probing at 590 nm (energy =  $1 \mu\text{J}$ ), using the Spectra-Physics picosecond laser system at the Rutherford Appleton Laboratory. Light diffusely reflected from the sample was detected by a filtered photodiode, and the signal fed to a Boxcar Integrator and thence to a IBM microcomputer. A second photodiode monitored a portion of the probe beam taken before hitting the sample, in order to correct for shot-to-shot variations in laser intensity.

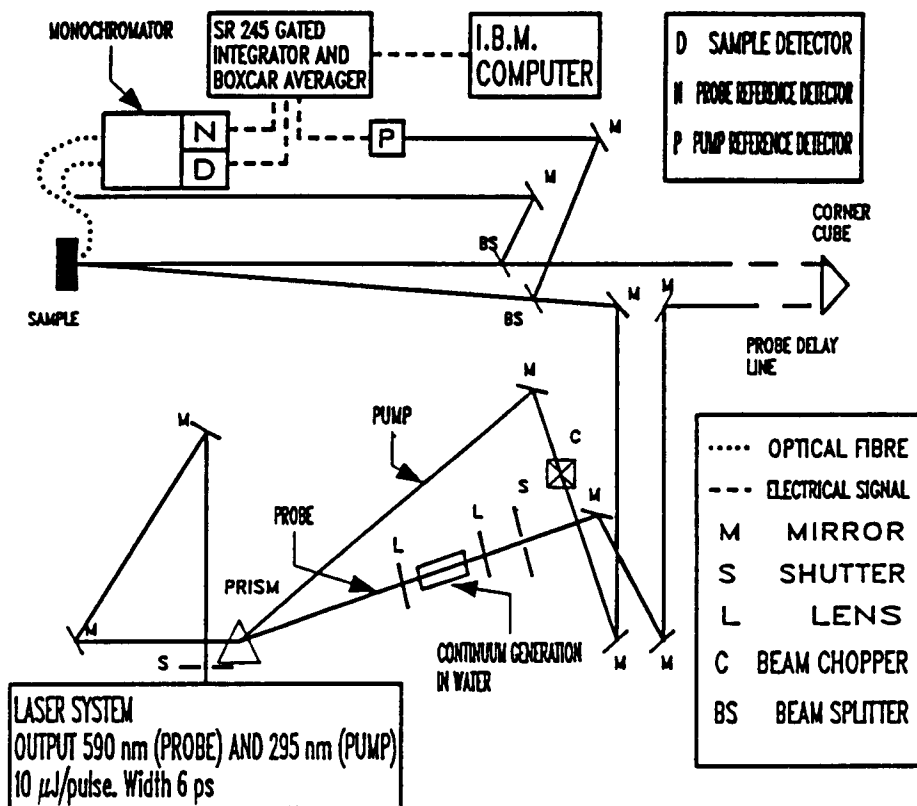


Figure 3. Schematic diagram of the optics and detection system employed in picosecond diffuse reflectance laser photolysis.

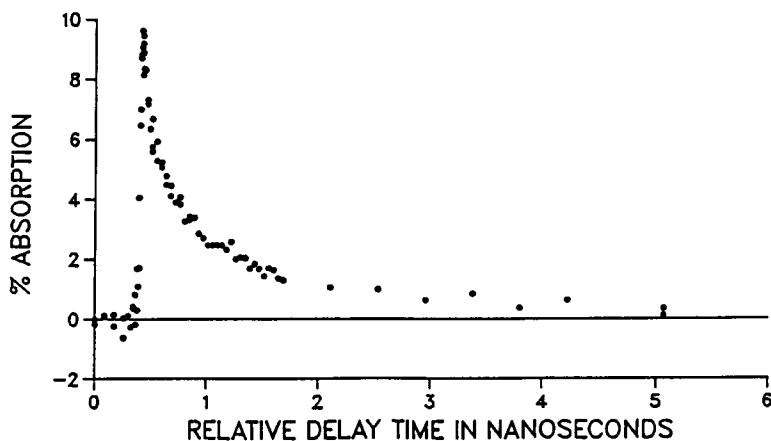


Figure 4. Transient absorption decay from a microcrystalline sample of 1,5-diphenyl-3-styryl-2-pyrazoline, using pump and probe wavelengths of 295 and 590 nm, respectively.

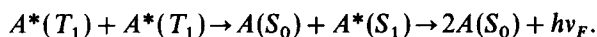
Samples are usually held in a powder holder behind a quartz window. Nearly collinear pump and probe beams were incident normal to the quartz window, with the pump beam about 2 mm in diameter and the probe beam located entirely within

the excited area of the sample. A portion of the diffusely reflected probe beam was detected by the photodiode. To record transient absorption (which is, strictly speaking, the relative decrease in diffuse reflectance), signals due to the probe beam alone and due to simultaneous pump and probe were obtained. Each run comprised 100 shots, and normalisation for shot-to-shot variation was carried out. Transient absorption following excitation at the pump wavelength reduces the level of the diffusely reflected probe beam to different extents for different delays between the pump and probe beams incident on the same area of sample. Experimental details are given elsewhere (Wilkinson *et al* 1986b). The transient absorption, illustrated in figure 4 for microcrystalline 1,5-diphenyl-3-styryl-2-pyrazoline, is assigned to the excited singlet of the pyrazoline (Wilkinson 1986).

### 3. Results and discussion

#### 3.1 Bimolecular reaction of adsorbed triplet acridine on silica surfaces

The nature and mobility of species present when acridine is adsorbed from high vacuum and dry solutions onto thermally pretreated silica and alumina have been investigated by ground and excited state spectroscopic techniques (Oelkrug *et al* 1989). On silica the main adsorbed species is hydrogen bonded acridine which upon excitation gives strong triplet-triplet absorption at 435 nm. The triplet state absorption for samples with very low coverage or high pre-treatment temperature has an exponential decay with a mean life-time of  $\sim 35$  ms and these samples show no delayed fluorescence. Mean lifetimes which approach this value are found only in perdeuterated acridine in organic host lattices (Kellman 1977) and the decay in fluid solutions is faster by about 2 orders of magnitude (De Mayo 1982). The high intensity of the transient signals in diffuse reflectance suggests that the triplet yield of the excited adsorbate and the extinction coefficient of the adsorbed triplet are similar to the solution values of 0.5 and  $2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , respectively. However, for samples of higher coverage or lower pre-treatment temperature the triplet decay is faster and non-exponential and delayed fluorescence is observed due to



The mechanism of elementary bimolecular interactions at interfaces is by no means fully understood. It can be a consequence of two-dimensional surface migration (diffusion) and bimolecular collisions or alternatively a three-dimensional interaction assuming an adsorption = desorption equilibrium. In order to clarify this problem we have studied a series of silica powders with particle sizes of about  $100 \mu\text{m}$  but with very different pore-diameters ranging from 6–100 nm. We have also varied the surface loading between 0.075 mg and 1 mg of acridine per g of silica. The effect of surface coverage on the rate of triplet decay when the surface has been preheated to  $< 300^\circ\text{C}$  is shown in figure 5. For such non-exponential decays we have evaluated the first half-life, i.e. the time taken for the absorption to reach 50% of the initial amount. These values show no correlation with volume concentration, there is however a clear correlation of the inverse of the lifetime with coverage.

A linear Stern-Volmer plot is obtained (see figure 6) when the inverse of the first half-life is plotted against surface coverage in the range from 1–7% suggesting that

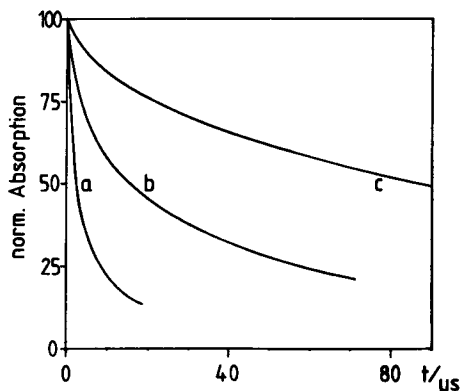


Figure 5. Normalised decay curves of triplet acridine on  $\text{SiO}_2$  fractosil 1000,  $\text{N}_2$  BET – surface area  $20 \text{ m}^2/\text{g}$ ,  $T_A = 100^\circ\text{C}$ , (a) 23%, (b) 7% and (c) 1.7% of a monolayer.

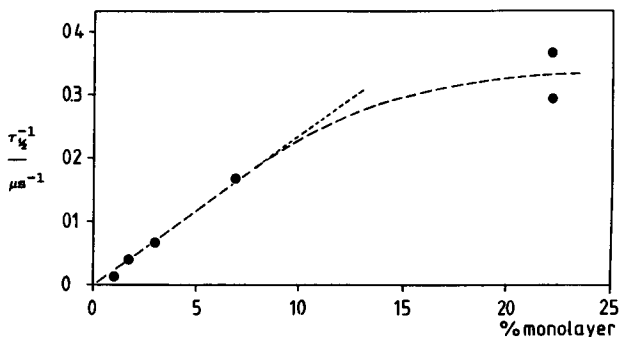


Figure 6. Dependence of the inverse of the first half-life for the decay of triplet acridine adsorbed on silica on surface coverage.

under these conditions bimolecular annihilation resulting from surface diffusion of triplet states is the predominant decay pathway. Calculations suggest that there is a high percentage conversion of ground state to triplet states for these samples. Assuming total conversion a two-dimensional bimolecular rate constant of  $2 \times 10^{14} \text{ dm}^2 \text{ mol}^{-1} \text{ s}^{-1}$  is obtained for triplet-triplet annihilation on silica pretreated at  $T_A < 300^\circ\text{C}$ . Higher preheating of the surface reduces the lateral mobility of triplet acridine and when  $T_A > 600^\circ\text{C}$  no migration is observed.

### 3.2 Radical ion-electron recombination following multiphoton ionisation of diphenylpolyenes on alumina

When excited at 354 nm physisorbed diphenylhexatriene, diphenyl butadiene, and chemisorbed stilbene give strong long-lived absorptions at 570, 540 and 480 nm respectively which deactivate on a time scale extending over more than 6 orders of magnitude with an extremely non-exponential decay. These transients are assigned as radical cations of the adsorbed diphenyl polyenes which decay by radical cation–electron recombination (Oelkrug *et al* 1988).

The ionisation potential of the diphenyl polyenes are such that the consecutive absorption of (at least) two photons at 354 nm is required to form these radical cations

and the dependence of the amount of transient on laser fluence confirms that more than one photon is required to produce the radical cations. The decay is explained as the temperature dependent recombination of the originally produced radical cation–electron pair.

#### 4. Conclusions

Diffuse reflectance laser flash photolysis has been shown to be a powerful method for studying photoinduced reactions at interfaces and within highly scattering samples. In this work we were able to measure a two-dimensional rate constant and to measure ion–electron recombination rates. It needs to be stressed that this technique can be applied to reactions in all types of heterogeneous systems as well as at gas/solid interfaces as discussed here. The ability to rapidly control the switching on of every type of elementary reaction of adsorbed species with pulsed lasers at interfaces and in other heterogeneous environments and to follow the resulting reactions is considerably enhancing the understanding of heterogeneous elementary reactions.

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