

Diffuse reflectance laser photolysis studies of the mechanisms of light-induced reactions in heterogeneous systems

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Abstract. The technique of diffuse reflectance laser flash photolysis is discussed and examples are given of time resolved spectra showing laser induced changes in diffuse reflectance and of transient decays as a function of time on timescales as short as a few picoseconds. Methods for extracting transient spectra and decay kinetics from raw experimental data are outlined. The application of the technique to the study of various heterogeneous systems including photochemical processes, within organic and inorganic microcrystals, within functionalised polymers and ion exchange resins, and to the laser photolysis of adsorbed species at interfaces and within zeolites are presented.

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

1. Introduction

Photochemical investigations in heterogeneous systems constitute a great challenge because of the potential such studies have for increased understanding of photobiology and of many technological applications of photochemistry. Heterogeneity makes the analysis of photochemical and photophysical data much more complicated than in homogeneous media but its major importance justifies efforts which are being made to cope with the inherent complexities. Recently we have extended to heterogeneous, opaque and often highly scattering systems the advantages of being able to subject them to flash photolysis investigation by using diffuse reflected light instead of transmitted light as the analysing source on timescales extending from several seconds (Kessler and Wilkinson 1981) to picoseconds (Kelly *et al* 1990a). Laser induced transient spectra and decay kinetics have been observed for a wide variety of samples including fractions of monolayers of organic molecules adsorbed on catalytic metal oxide surfaces (Oelkrug *et al* 1987, 1989) and included within zeolites (Kelly *et al* 1990c) from semiconductor powders (Wilkinson *et al* 1986c) and porous electrodes doped and undoped (Kossanyi *et al* 1990), from ruthenium(II) complexes within ion exchange resins (Masschelin *et al* 1991), from organic microcrystals (Wilkinson and Willsher 1984), and from organic dyes adsorbed on microcrystalline cellulose (Wilkinson *et al* 1991, 1992), on fabrics and chemically bound to polymers (Bourdelande *et al* 1988; Kelly *et al* 1990b), from paper pulp (Schmidt *et al* 1990), and from photographic emulsions (Wilkinson and Leicester 1992). Other groups are now

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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

2.1 Nanosecond diffuse reflectance flash photolysis

The equipment used for nanosecond 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 typically as shown in figure 1. Samples are often held in a powder holder behind a quartz window or in a sealed fluorimeter cell. The observable in diffuse reflectance laser flash photolysis is $\Delta R(t)$ defined as follows:

$$\Delta R(t) = [R_b - R(t)]/R_b, \quad (1)$$

where R_b is the sample reflectance before exposure to the exciting laser pulse and $R(t)$ the reflectance at time t after excitation. ΔR is thus the fractional change in reflectance and $100 \Delta R$ is often referred to as the percentage absorption by the transient.

Figure 2 shows the four traces which are recorded at each analysing wavelength necessary to obtain a corrected trace of reflectance change $\Delta R(t)$ as a function of time. The four experimental traces are: (1) baseline trace i.e. analysing light reflected from sample in the absence of laser excitation; (2) absorption trace i.e. analysing light reflected from sample before (pretrigger) and after laser excitation. This shows a decrease in reflection due to absorbing transients; (3) emission trace i.e. any emission caused by laser excitation in the absence of analysing light; (4) zero trace i.e. the digitiser is triggered in the absence of either laser excitation or analysing light to establish the zero settings. From these four traces a corrected trace of the reflectance change as a function of time can be obtained at each analysing wavelength. Time resolved spectra are obtained by measuring many such traces at different wavelengths and

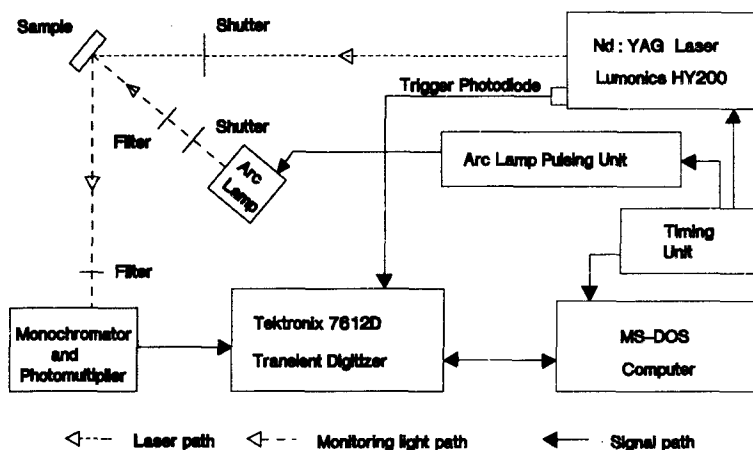


Figure 1. Apparatus for diffuse reflectance laser flash photolysis.

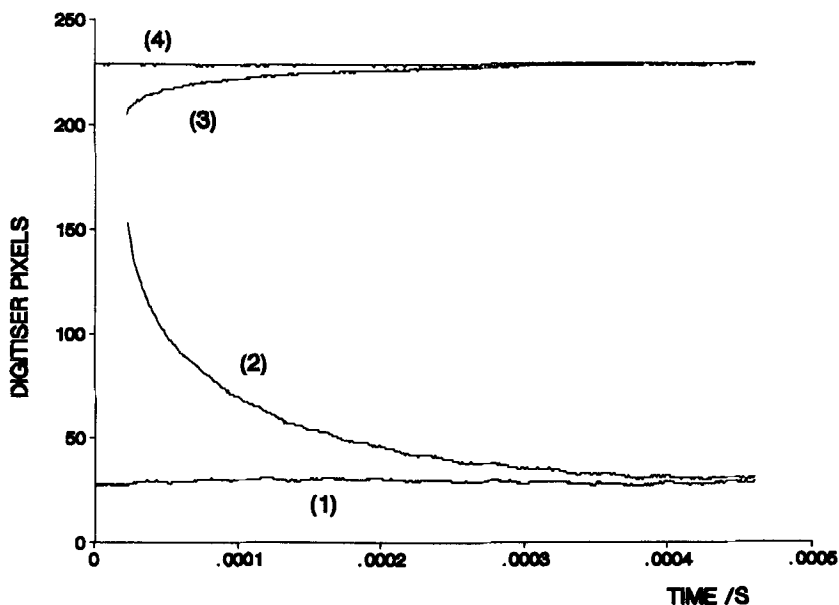


Figure 2. Data traces recorded for microcrystalline benzil exciting at 354 nm and analysing at 510 nm. (1) Baseline (lamp only), (2) transient (lamp and laser), (3) emission (laser only), (4) top line (no light).

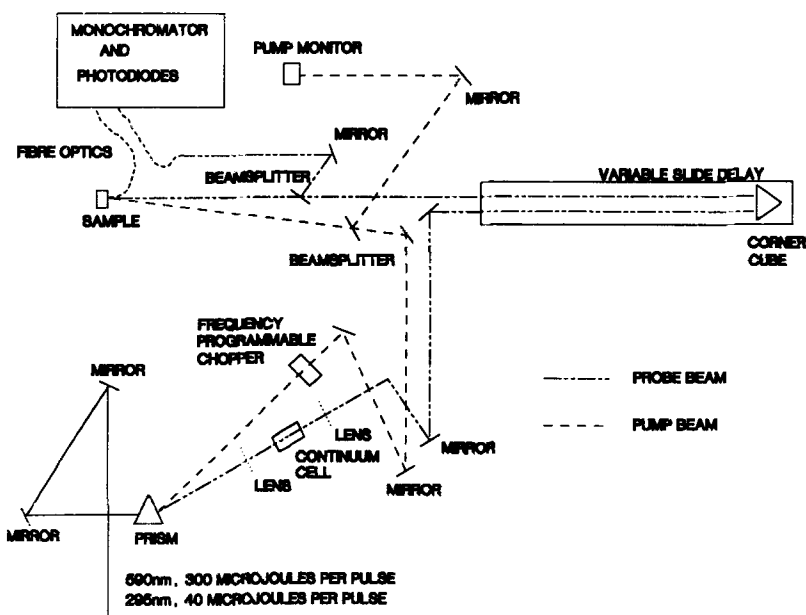


Figure 3. Picosecond diffuse reflectance pump-probe laser photolysis apparatus.

then plotting the magnitude of the reflectance change as a function of wavelength at a known delay (see later). Full experimental details are given in the references (Wilkinson 1986; Wilkinson and Kelly 1990; Wilkinson and Willsher 1990).

2.2 Picosecond diffuse reflectance flash 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 (Wilkinson *et al* 1986b; Kelly *et al* 1990). Generation and detection of the transient absorption was effected by pumping the sample at 295 nm (pulse width = 6 ps, energy = 20 μ J) and probing at 590 nm (energy = 1 μ 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.

Samples are usually held in a powder holder behind a quartz window. Nearly co-linear pump and probe beams are 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

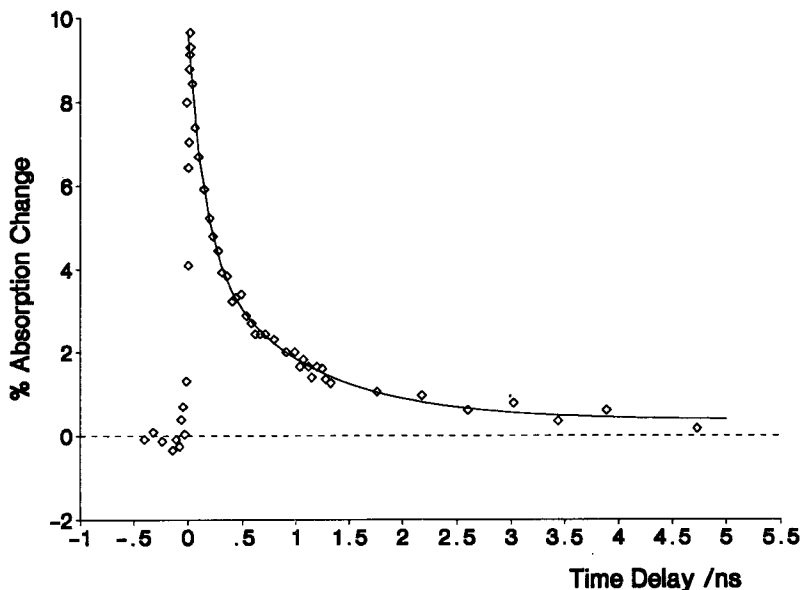


Figure 4. Decay of transient absorption for microcrystalline 1,5-diphenyl-3-styryl-2-pyrazoline (corrected for emission).

incident on the same area of sample. Thus unlike our nanosecond studies we have found it necessary to accumulate at least one hundred pump-probe shots at each delay in order to obtain each point shown on a decay curve. The transient absorption, for microcrystalline 1,5-diphenyl-3-styryl-2-pyrazoline illustrated in figure 4 is assigned to excited singlet states of the pyrazoline (Kelly *et al* 1990). The observed transient decay curve can be fitted using a biexponential model with lifetimes of 1.6×10^{-10} and 1.3×10^{-9} seconds for the faster and the slower decay components respectively. Full experimental details are given elsewhere (Kelly *et al* 1990).

2.3 Data analysis of transient changes in diffuse reflectance

More extensive discussions of the analysis of data are given elsewhere (Kessler *et al* 1983; 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

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

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

$$dJ(x) = J(x)(K + S)dx - J(x)Sdx \quad (3)$$

The diffuse reflectance R is given by

$$R = J_0/I_0 \quad (4)$$

where I_0 and J_0 are the incident and reflected fluxes at the surface. Equations (2) and (3) 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

$$(1 - R)^2/2R = K/S = F(R). \quad (5)$$

$F(R)$, the emission 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 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 (Kessler *et al* 1983; Oelkrug *et al* 1987) 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, these are illustrated schematically in figure 5, curves 1 and 4, respectively.

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 (Kubelka 1948). For optically thick samples at analysing wavelengths where only the transient absorbs, the remission function given by (5) is a linear function of the concentration and can be used for kinetic analysis and for plotting absorption spectra. For the low

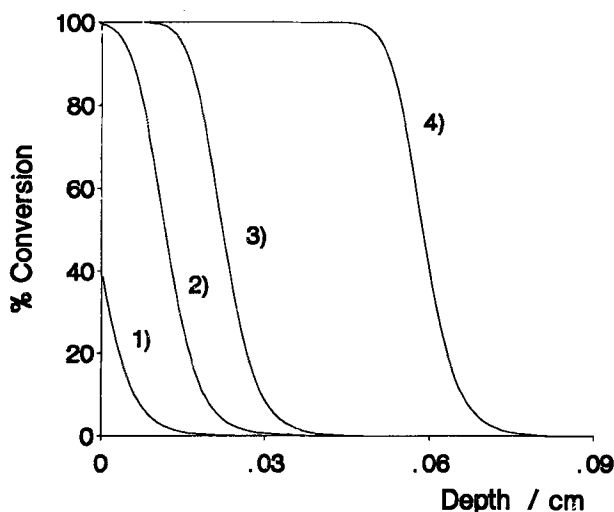


Figure 5. Plot showing percentage conversion of ground state molecules as a function of sample depth with increasing laser intensity.

percentage conversions, the concentration of transients decreases exponentially below the irradiated surface. This occurs when there is a high concentration of ground state absorbers and with low laser fluences. An analytical solution for the change in reflectance expected has been obtained (see Lin and Kan 1970) and is in the form of a converging series which has been shown (Kessler *et al* 1983) to relate ΔR as a linear function of the concentration of transient at values of ΔR less than 0.1. Between these two limiting cases the change in ΔR with concentration depends on the concentration profile below the irradiated surface. In order to establish if either of the two limiting cases pertain, it is necessary to calculate the expected change in transient concentration as a function of distance below the irradiated surface.

2.4 Calculation of transient concentration profiles

To extract kinetic information from $\Delta R(t)$ one must first understand the concentration profile. A detailed description of the modelling procedure, including all relevant equations, has been published (Kessler *et al* 1983; Oelkrug *et al* 1987). A brief outline of the algorithm is given below.

(1) The sample is divided into a large number of thin slices i , such that the concentration of the ground-state absorbers stays constant within each individual slice. When the procedure starts (before the sample is subjected to laser excitation) the concentration of ground state absorbers, A , in each of the slices is $A_i = A_0$, the initial concentration of ground-state absorbers. The absorption coefficient at the laser wavelength is given by $K_{\lambda,i}^e = 2\epsilon_A^e A_i$ where ϵ_A^e is the extinction coefficient of A at the excitation wavelength. Usually it is assumed that the transient does not absorb significantly at the laser wavelength and that the scattering coefficient S is independent of wavelength.

- (2) The laser pulse which excites the sample is divided into portions Δt where Δt is generally 1/100 of the total pulse duration.
- (3) The sample is considered as having been irradiated with a portion Δt of the laser pulse. The concentrations of transient species, T_i , formed in each slice because of light absorption are determined, and a new set of ground-state concentrations, A_i , are calculated. In general, after the sample has been exposed to a portion of the laser light, the concentrations A_i are no longer equal, due to the attenuation of the exciting pulse as it passes through the sample. Mass conservation requires that $A_i + T_i = A_0$ in all slices.
- (4) Using the new values of A_i , new absorption coefficients $K_{A,i}^e$ are calculated for each slice.
- (5) The procedure recycles to step (3), and the next portion of the laser pulse is considered to irradiate the sample.
- (6) When all of the laser pulse has irradiated the sample, the concentration of ground state absorbers A_i and the concentration of transient species T_i in each slice are known. Steps (1) through (6) generate the transient concentration profile. To calculate ΔR at an appropriate analysing wavelength the following additional steps are performed.
- (7) Estimates of the extinction coefficients at the *analysing* wavelength for the transient species, ϵ_T^a are used to calculate the absorption coefficients in each slice due to the ground-state absorbers $K_{A,i}^a = 2\epsilon_A^a A_i$, and transient species, $K_{T,i}^a = 2\epsilon_T^a T_i$.
- (8) The reflectance of each slice, R_i , can now be calculated using the absorption coefficients $K_{A,i}^a$, $K_{T,i}^a$ and the scattering coefficient S .
- (9) Finally, the individual reflectances R_i are combined using a recursion formula to give the expected reflectance of the sample.

If the absorption coefficient K is in excess of 10^4 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 rise (see Wilkinson *et al* 1986c). We have not only shown how to predict any temperature rises but have confirmed our calculations by measurements in the case of TiO_2 . The possibility of large temperature rises has always to be borne in mind and lower laser fluences, lower concentrations or excitation into weaker bands must be employed where necessary to avoid thermal effects. It is important to stress that when the penetration depth of the exciting light is $> 0.1 \text{ mm}$, temperature rises in opaque samples using our nanosecond laser system are negligible i.e. $< 1^\circ\text{C}$.

3. Results and discussion

3.1 Laser photolysis at interfaces and within zeolites

Kessler and Wilkinson (1981) studied various aromatic hydrocarbons chemisorbed on γ -alumina. The samples were adsorbed at less than monolayer levels, and the transient spectra observed were shown to be due to triplet-triplet absorptions. We have been attempting to make such studies in order to explore the electronic structures, excited state spectra and lifetimes of adsorbates. We are also interested in energy, electron and proton transfer of photoexcited species at interfaces (Wilkinson and Ferreira 1988; Oelkrug *et al* 1991).

We have also studied radical reactions on surfaces, for example, the α -cleavage of 1,1,3,3-tetraphenylacetone (TPA) has been used as a source of diphenylmethyl radicals in our experiments (Kelly *et al* 1990c). The production of the second diphenylmethyl radical via decarbonylation of the initially produced diphenylacetyl radical occurs rapidly and thus, provides an efficient and practically instantaneous source of two diphenylmethyl radicals per ketone molecule as shown below.



The three solid supports used in these experiments differ considerably in their properties. Silica gel is a porous surface with, in our case, an average pore size of 6 nm and a surface area of 480 m²/g. Both silica gel and Silicalite contain only silicon and oxygen, although the latter is hydrophobic whereas the former has a large amount of physical adsorbed water on the surface. The structure of the aluminosilicate NaX zeolite comprises a three-dimensional network of relatively large cavities or supercages (– 1.2 nm) connected by 0.7 – 0.8 nm pores or channels. The Si/Al ratio of approximately 1.5 results in a large proportion of exchangeable cations (in our case Na) and a strongly hydrophilic zeolite. It should be noted that TPA can easily fit within the pore structure of silica gel and the channel system of NaX. However, the relatively small channels of Silicalite result in adsorption of TPA only on the external surface, although the photoproducted diphenylmethyl radical may migrate into the channels. For all the three supports diphenylmethyl radicals are produced with a characteristic absorption maximum at 335 nm (e.g. see figure 6) which decays over timescales which vary from hundreds of nanoseconds to minutes (for a full discussion see Kelly *et al* 1990c).

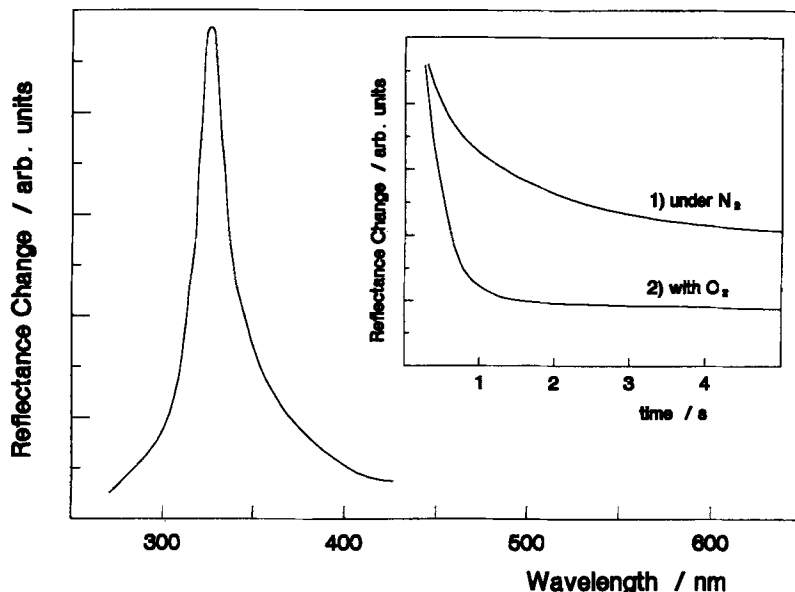
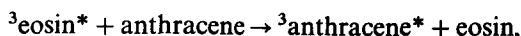


Figure 6. Transient spectrum of diphenylmethyl radicals produced by 266 nm excitation of 3% coverage of tetra-phenylacetone on silica. Inset shows transient decays monitored at 340 nm.

It also is of interest to compare those processes which can occur in both homogeneous and heterogeneous environments. For example, we have studied energy transfer at surfaces (Wilkinson and Ferreira 1988) and in homogeneous solution. Energy transfer on cellulose surfaces shows substantial static quenching which approaches a Perrin-type behaviour which contrasts with the situation in homogeneous solution where dynamic quenching yields Stern–Volmer kinetics (Wilkinson and Ferreira 1988). On silica dynamic quenching is also observed for example between eosin and anthracene due to the process



for example, see figure 7 (Wilkinson *et al* 1992).

The nature and mobility of the species present when acridine is adsorbed from high vacuum onto thermally-pretreated alumina and silica have been investigated by ground and excited state spectroscopic techniques (Oelkrug *et al* 1989). For alumina treated at high temperatures ($> 500^\circ\text{C}$) σ -bonded acridine is the main species present, while the acridinium cation AH^+ predominates at lower activation temperatures (100°C). The triplet–triplet absorption of AH^+ at 480 nm has been directly observed without a triplet sensitiser, and the decay is non-exponential. On silica the main adsorbed species is hydrogen bonded acridine which shows triplet–triplet absorption at 435 nm and which, for samples of low coverage or high pre-treatment temperature, has an exponential decay with a lifetime of about 35 ms. For samples of high coverage or low pre-treatment temperature, the triplet decay is faster and non-exponential, and delayed fluorescence is observed. This arises from triplet–triplet annihilation, a consequence of the mobility of acridine on the silica surface for which the two-dimensional bimolecular rate constant is $8 \times 10^{13} \text{ dm}^2 \text{ mol}^{-1} \text{ s}^{-1}$.

No delayed fluorescence occurs when silica has been pre-treated at high temperatures, conditions which favour dehydroxylation of the surface to form siloxan units. These have a high activation barrier to translational motion and thereby impede the lateral mobility of the adsorbate. For alumina, the nature of the surface permits virtually no mobility of the acridine, and hence no significant bimolecular processes are observed on this adsorbent (see Oelkrug *et al* 1989).

Organic photoreactions on zeolite supports have become an area of increasing interest in the last few years (Casal and Scaiano 1984). A study of the ketone, xanthone, included within the hydrophobic zeolite Silicalite has yielded some very interesting information relating to the host environment (Wilkinson *et al* 1986c). Silicalite is over 99% SiO_2 and consists of a system of near-circular zig-zag channels, cross-linked by elliptical straight channels (Flanagan *et al* 1978). The xanthone transient was assigned as the triplet, showing a characteristic maximum at 605 nm.

It is well-known (Garner and Wilkinson 1976) that the absorption maxima of triplet xanthone is sensitive to the solvent polarity and the value obtained for λ_{max} would be indicative of a polar environment in dilute solution. Since Silicalite is a hydrophobic matrix this is somewhat surprising, however, it may indicate that xanthone is adsorbed on the walls of the channels. Another observation made was that the decay process extends over a considerable timescale from ns to ms. This suggests a variety of lifetimes for this ketone triplet at different surface sites. The growth of this transient on picosecond timescales constituted the first reported example of picosecond diffuse reflectance laser photolysis (Wilkinson *et al* 1986b).

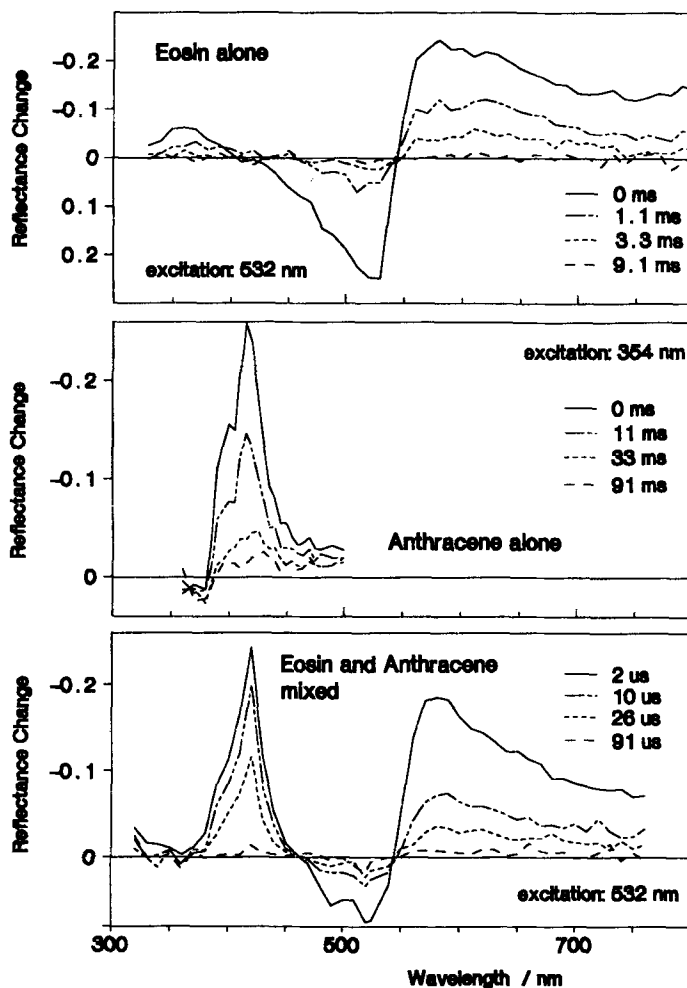


Figure 7. Transient absorption spectra illustrating energy transfer between eosin and anthracene on silica.

3.2 Functionalised polymers

The idea of anchoring a photosensitizer to an insoluble polymer support has become widespread. The technique of diffuse reflectance flash photolysis allows one to monitor excited state lifetimes and the production and decay of other transient species. In collaboration with Professor J Font from the Autonomous University of Barcelona, Spain, we have carried out several studies (Wilkinson *et al* 1987; Bourdelande *et al* 1988) to obtain evidence concerning intermolecular and intramolecular energy transfer in insoluble polymeric benzophenone and from ruthenium *tris*(2,2'-bipyridine) bound to insoluble polymers. The transient absorption spectra are similar to those observed for ruthenium *tris*(2,2'-bipyridine) in dilute fluid solution. Experiments using methyl viologen as quencher show that quenching of excited states is forty times slower than in aqueous solution (Bourdelande *et al* 1988).

3.3 Ion-exchange resins

We have also compared the photophysical properties of $\text{Ru}(\text{bpy})_3^{2+}$ incorporated into an ion exchange resin sephadex SP C25 with its properties in aqueous solution. Other potential photosensitizers investigated include the three complexes $\text{Ru}(\text{bpy})_n(\text{TAP})_{3-n}$ where $n = 0, 1$ and 2 and TAP represents 1,4,5,8-tetraazaphenanthrene.

The partial immobilisation of the complexes in the cavities of the sephadex leads to two opposing effects (i) quenching by the sephadex and (ii) an increase in luminescence lifetimes. The quenching by the sephadex is shown to involve a statistical factor depending on the number of TAP ligands on the complex and on the geometry and size of the cavities in the resin. Full details are given in Masschelein *et al* (1991).

4. Conclusions

In these studies of 'Nanosecond and Picosecond Laser Photolysis of Opaque Heterogeneous Photosensitizers', we have been able to demonstrate the utility of the technique of diffuse reflectance to enable transient spectra and decays to be obtained from many dyes or sensitizers in a variety of heterogeneous environments. Considerable progress has been made in understanding why the technique is so sensitive and computer simulation demonstrates how kinetic parameters can be obtained. Since many heterogeneous systems give a distribution of decay constants it is not usually possible to quote a single decay constant for a heterogeneous system. However, the nature of the distribution of decay constants can be determined.

In several of the photochemical processes investigated, such as photoinduced reactions at interfaces, within zeolites, dyed fabrics and doped semiconductors, we have been able to obtain results concerning intermediates and mechanisms which cannot be obtained by any other method. Many of the studies reported above open up whole new areas for investigation. We also have obtained unique information on the translational mobility, intramolecular and bimolecular photoreactions of adsorbates on metal oxide surfaces.

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