

THE STUDY OF TRANSIENT ABSORPTIONS IN OPTICALLY DENSE MATERIALS BY DIFFUSE REFLECTANCE LASER FLASH PHOTOLYSIS[†]

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(Received August 29, 1984)

Summary

The production and analysis of transient absorptions in highly scattering opaque materials, as detected by measuring the change in the level of the diffusely reflected monitoring light following pulsed excitation, are discussed. Examples of transient absorptions obtained by this means are given for samples of organic microcrystals, powdered semiconductors and polymer-bound Rose Bengal.

1. Introduction and historical background

Flash photolysis has proved to be a very powerful and important technique in the study of primary photoprocesses by allowing the study of transient absorptions [1]. Its use, however, has been hitherto restricted to samples which are transparent, since changes in the *transmitted* monitoring light following absorption by the transient are detected and analysed. The technique of diffuse reflectance laser flash photolysis, currently being developed at the University of Technology, Loughborough, employs *diffusely reflected* monitoring light to investigate transient absorptions, and thus can considerably extend the scope of flash photolysis by permitting the direct study of non-transparent samples.

The first reported transient absorptions detected by measuring changes in the diffusely reflected monitoring light following pulsed excitation were published in 1981 [2]. These results were obtained by employing a millisecond flash-lamp as the excitation source and the materials studied were a number of aromatic hydrocarbons chemisorbed on γ -alumina. Transient absorptions within microcrystalline ZnO and chromium-doped LaAlO₃ [3] were then reported in a second publication. The samples used in these

[†]Paper presented at the Xth IUPAC Symposium on Photochemistry, Interlaken, Switzerland, July 22 - 27, 1984.

pioneering experiments yielded transient absorptions of the order of only a few per cent, and the duration of the millisecond flash was a limitation in the detection of fast transients in other samples. In order to exploit the full potential of the technique an apparatus capable of studying absorptions which decay in the nanosecond-to-microsecond time domains was constructed during 1981 and 1982.

2. Instrumentation

As with transmission flash photolysis, the important features of any apparatus designed to study transient absorptions are the production of the transient state, its subsequent detection by the analysing light and the capturing and/or storing of its decay. The only major difference with analysing in the reflectance mode is the means of monitoring the decay. The essential features of an apparatus to undertake diffuse reflectance laser flash photolysis studies are very similar to those of instrumentation designed for transmission work. An outline of the components of our apparatus is as follows. Excitation of the sample is achieved by one of the harmonics of a pulsed Nd-YAG laser (J.K. Lasers Ltd.). The pulse duration is 20 ns, and the maximum available energies of excitation are 200 mJ pulse⁻¹ at 532 nm, 40 mJ pulse⁻¹ at 354 nm and 15 mJ pulse⁻¹ at 266 nm. If other wavelengths of excitation are required these are obtainable by pumping a pulsed dye laser with the YAG laser. The sample is monitored with light from a pulsed 250 W xenon arc lamp (pulse width, 0.5 ms) (Applied Photophysics Ltd.) or with a CR-2000 K continuous wave laser (Coherent Ltd.) which pumps a dye laser. The monitoring light, diffusely reflected from the sample, passes through a monochromator (Applied Photophysics Ltd.; *f*/3.4 grating) and is detected with an R928 photomultiplier (Hamamatsu Ltd.). The signal from the photomultiplier is taken to a Tektronix 7912 AD programmable digitizer. The geometric arrangement of the sample, the exciting and analysing beams and the monochromator entrance will be discussed in detail in Section 3. A Minc PDP 11/03 minicomputer is employed to coordinate the sequence of events to obtain the transient absorption (laser firing; shutter control; pulsing of the arc lamp; driving of the monochromator grating; setting, triggering and reading of the digitizer). In addition, the minicomputer performs kinetics analyses on the transients and provides hard copies on a Tektronix 4662 plotter. The method of analysis will be discussed later.

3. Geometric arrangement of sample and exciting-analysing light

In dealing with reflected light from an opaque material, a differentiation has to be made between the specular and the diffuse reflection. In the former case, the incident light is reflected from the surface with the angle of reflection equal to the angle of incidence, and this "mirror"-type specular

reflection has not significantly penetrated the material. In the latter case, the sample has undergone substantial penetration and, if part of the incident light has been absorbed by the sample, then its diffuse reflection can be used to monitor the absorption. We find that the specular reflection contains little information on any such absorption, and thus it is not detected.

The geometric requirements of the sample, the monochromator entrance and the analysing light have to be such that no specularly reflected monitoring light enters the monochromator, while the maximum amount of the diffuse reflection is gathered. On introduction of the exciting pulse, two further conditions must be met: (i) the exciting pulse should be coincident with the area of sample that receives the monitoring light and (ii) its reflection (specular and diffuse) must not interfere with the detection of the diffusely reflected monitoring light. The resultant geometric arrangement is described with reference to Fig. 1. The arc lamp is positioned normal to the sample face, so that the incident beam and specular reflection of the monitoring light are coincident. (The sample is contained in a powder holder behind a fused silica window, with the depth of sample being about 1 mm.) The exciting pulse is incident on the sample at an angle of 45° , and thus its specular reflection occurs at 45° to the sample face. These two beams are arranged to be coincident on the sample so that the area receiving the exciting laser pulse is slightly larger than the area being monitored. This is to ensure that *all* the diffusely reflected analysing light has probed the exciting laser pulse is slightly larger than the area being monitored. This is and analysing light is about 1 cm^2 . A monochromator is placed such that the laser specular reflection misses its entrance and such that the diffusely reflected monitoring light, concentrated by a lens (focal length, 8 cm), gives

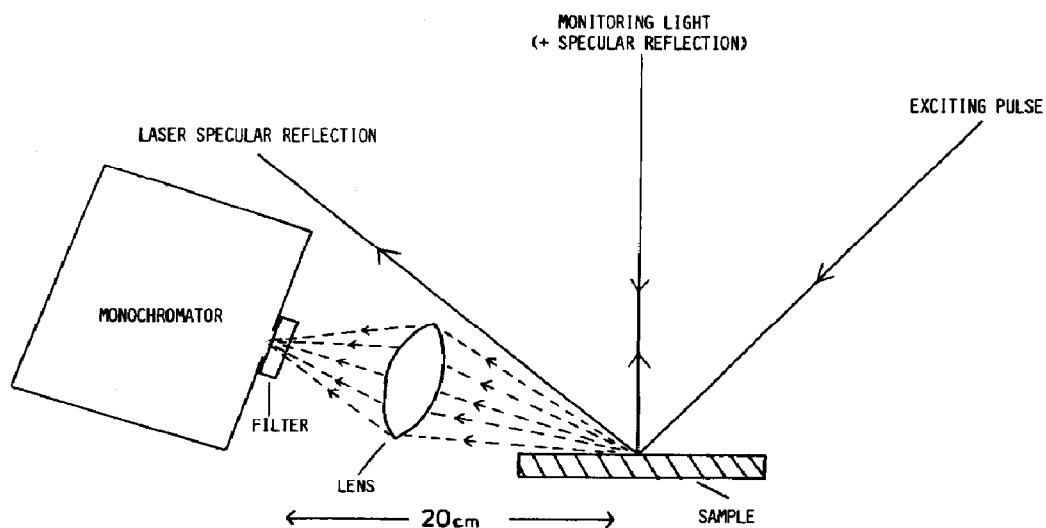


Fig. 1. Schematic diagram of the geometry of the sample and of the exciting and monitoring beams used to produce and detect transient absorptions in a light-scattering sample.

an optimum signal. The filter at the monochromator entrance is required to remove the diffuse reflection of the laser. For excitation at 354 nm, a solution of biphenylene in benzene is employed and, for 532 nm, an aqueous solution of cobalt sulphate is used. It is essential to prevent all scattered laser light from entering the monochromator and the photomultiplier. Failure to do so can result in the generation of spurious signals by the overloading and recovery of the photomultiplier. It is equally important that the filters themselves do not luminesce, as this will be detected by the photomultiplier. The geometric arrangement described above was arrived at by trial and error and by the constraints of space on the optical bench. By varying the angles of incidence of the exciting and monitoring beams other geometric dispositions are obtained which also permit detection of transient absorptions, but no significant improvement in the size of the transient signal was observed. It was found that using an integrating sphere offered no substantial improvement in the size of the transient signal.

4. Analysis of transient absorptions: spectra and kinetics

As was mentioned earlier in Section 2, the on-line minicomputer performs the task of analysis of transient absorptions obtained from the sample. The level of diffusely reflected monitoring light is recorded both in the presence and in the absence of laser excitation; in the absence of the laser, a reproducible signal, constituting a perfect blank, is obtained. In the presence of the laser, the transient absorption results in a decrease in the diffusely reflected monitoring light. Luminescence, if any, induced by laser excitation alone is also recorded, and the transient absorption is then corrected by the computer for luminescence and for any reproducible irregularities in the blank. The three traces which are thus obtained and stored in the minicomputer are depicted in Fig. 2 for microcrystalline benzil. Trace a is the diffusely reflected signal of the monitoring light from the unexcited sample, trace b is the luminescence from the sample resulting from laser excitation alone and trace c is the uncorrected transient absorption produced by simultaneous irradiation of the sample by the laser and the arc lamp. The corrected transient absorption obtained from these three traces is then ready for analysis.

For the kinetics analysis and spectral interpretation, the relationship between the change in the level of the diffusely reflected monitoring light following excitation (*i.e.* the transient absorption and its decay) and the concentration of the absorbing species must be ascertained. To analyse transient absorptions in the transmission mode, the Beer-Lambert law is normally used to relate the absorbance of the excited state to the fraction of the monitoring light which is absorbed. This is depicted schematically in Fig. 3(a), where a non-scattering optically transparent sample receives exciting and monitoring light at right angles. For an optically dense sample such as that being studied by diffuse reflectance laser flash photolysis, no

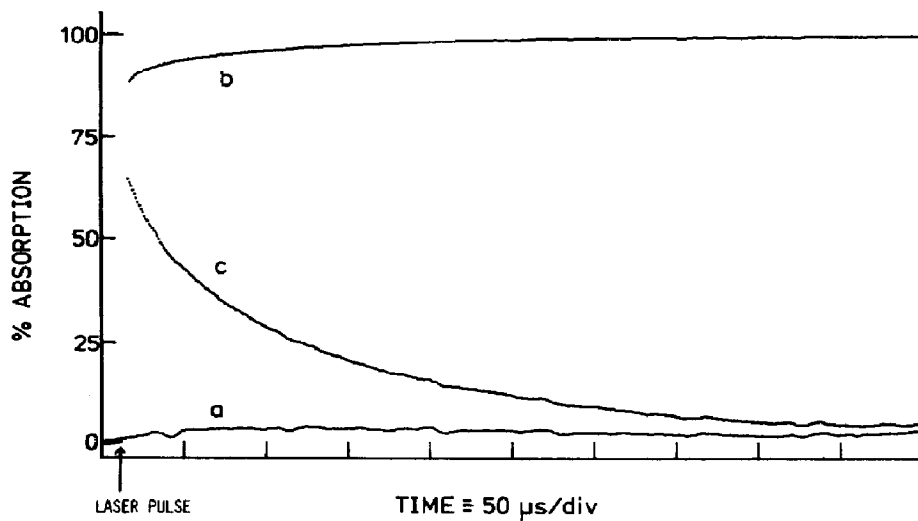


Fig. 2. The three signals taken from a sample of microcrystalline benzil to obtain a corrected transient state absorption: trace a, diffusely reflected monitoring light from the unexcited material; trace b, luminescence resulting from laser excitation; trace c, diffusely reflected monitoring light from the excited sample.

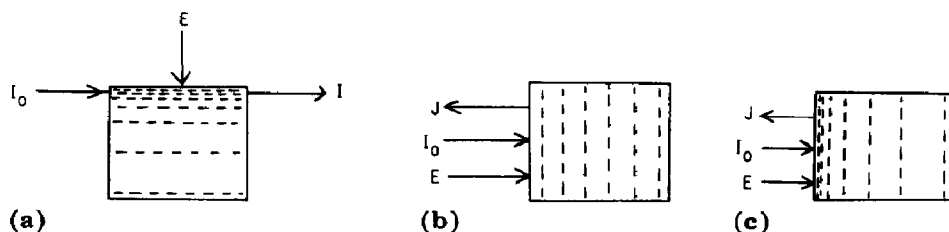


Fig. 3. Schematic diagrams for transient production and analysis in media with different absorbing and scattering properties (E , exciting light; I_0 , incident monitoring light; I , transmitted monitoring light; J , reflected monitoring light): (a) transparent medium, with excitation at right angles to the analysis ($A = \log(I_0/I)$); (b) light-scattering medium, in which a homogeneous concentration of transient is produced in the volume of sample monitored by the analysing light ($R = J/I_0$, $K/S = (1 - R)^2/2R$, where R is the reflectance, K is the absorption coefficient and S is the scattering coefficient); (c) light-scattering medium, where an exponentially falling-off concentration of transient is produced in the analysed volume of the sample ($R_b - R \propto C$, where R_b is the background reflectance).

light is transmitted. Two cases can be identified: one is depicted in Fig. 3(b), where excitation induces a homogeneous concentration of excited states in the volume of sample monitored by the analysing beam, and the other is depicted in Fig. 3(c), where an exponentially falling-off concentration of excited states is produced in a similar volume of sample. The former case is likely to be encountered in very thin samples or with a large penetration depth of exciting light, and the Kubelka-Munk function [4] can be employed to relate the reflectance R (the ratio of the reflected light intensity J to the incident light intensity I_0) to the absorption coefficient K and the scattering coefficient S of the sample:

$$\frac{(1 - R)^2}{2R} = \frac{K}{S}$$

K is proportional to the concentration of the absorbing species.

It is believed that case c, where an exponentially falling-off concentration of excited states is probed by the monitoring light, prevails in the experimental conditions employed to produce and detect the transient absorption. The system can be thought of as a series of "thin slices" for which the Kubelka-Munk function applies. Summing the individual reflectances from each slice should predict the value of R for the entire sample. This approach, plus the numerical solution of the differential equations governing the incident and reflected intensities of "slices" of sample at various depths in the material, has been successful in predicting that a linear relationship exists between the change in reflectance and the transient concentration, provided that the reflectance changes by less than 10% [5]. This prediction was arrived at by choosing appropriate values for the absorbing and scattering coefficients and for the reflectances at the exciting and analysing wavelengths. The conclusions drawn in ref. 5 are very important for the analysis of transient absorptions obtained by diffuse reflectance laser flash photolysis and are summarized in Fig. 3(c), where the value of the difference $R_b - R$ between the background reflectance and the transient reflectance is directly proportional to the concentration C of the absorbing species.

The first experiments with the new apparatus employed samples of microcrystalline benzophenone [6] and benzil [7] which yielded transient absorptions well in excess of 10% (see also Fig. 2 for benzil). While it was extremely pleasing to be able to detect such large signals, it was also a little disturbing that the theory predicted that only the portion of the decay smaller than 10% could be analysed by taking a direct proportionality between the signal size and the transient concentration. However, with this proportionality assumed, the entire decay was analysed and it was discovered that a very close correlation existed between the absorption and the phosphorescence decays of each individual material. Since it is quite certain that the same transient is being monitored by both its emission and its absorption, this correlation in decays leads to the assumption that the linear relationship between the size of the transient absorption and the excited state concentration still holds for signals greater than 10%, at least for benzophenone and benzil.

Kinetics analysis and spectral interpretation can now be undertaken by the minicomputer and will now be discussed with reference to Fig. 2. The monitoring light recorded immediately before the laser fires is termed the pre-trigger (this is the portion to the left of the time at which the sample is excited (see trace c)). The size of the absorption, the difference ΔI between any point of the corrected decay and the pre-trigger, is proportional to the concentration of the transient species, and the kinetics analysis for the first-order process and the second-order process is performed by least-squares fitting of $\log(\Delta I/\Delta I_0)$ versus time and of $\Delta I_0/\Delta I$ versus time respectively,

where ΔI_0 is the initial value of ΔI immediately following laser excitation. Spectral interpretation of the transient data is achieved by taking a series of absorptions at different monitoring wavelengths and then plotting the percentage absorptions taken at the same given times after the laser pulse against the monitoring wavelength.

5. Some experimental results obtained by diffuse reflectance laser flash photolysis

It has already been mentioned in Section 4 that samples of benzophenone and benzil in microcrystalline form have been studied. The spectra of the transient absorptions were very similar to the triplet-triplet absorption spectra of the compounds in a fluid solution (see refs. 6 and 7) and thus the absorptions detected in the diffuse reflectance mode were assigned as triplet-triplet absorptions. Their decays followed a mixture of first- and second-order kinetics, with the former predominating in benzil and the latter predominating in benzophenone. Decays of the phosphorescence of each material followed the same kinetics pathway, within experimental error. The half-lives of the decay of the transients were 5 μs and 50 μs for benzophenone and benzil respectively.

Having successfully detected and analysed the triplet-triplet absorptions in benzophenone and benzil, we studied other classes of materials. Samples of powdered undoped semiconductors (TiO_2 , WO_3 , ZnO and CdS) gave substantial transient absorptions (greater than 30%) which occurred close to the band gap of the material [8]. The semiconductors were excited at 354 nm, which corresponds to ultra-band-gap wavelengths of the materials. The long-lived luminescence from the semiconductors was extremely weak. The half-lives of the absorptions are of the order of 2 μs for TiO_2 , 8 μs for ZnO , 20 μs for CdS and 50 μs for WO_3 . Transition-metal-doped ZnO pellets, used as electrodes in photoelectrochemical studies, were found to give transient absorptions when excited at 532 nm, which are believed to be assignable to the metal dopant [9]. It is considered that the ability to study transient absorptions in semiconducting materials will be of immense use in further understanding the light-induced processes which occur when they act as light-sensitive electrodes in photoelectrochemical cells, or when they act as photocatalysts.

Another group of compounds which have interesting photochemical properties are dyestuffs. Many practical applications of these materials require their use in a non-transparent form and, to determine whether transient absorptions were detectable in the diffuse reflectance mode, Rose Bengal was subjected to study. Particular interest in Rose Bengal exists due to its behaviour as a sensitizer for singlet oxygen production [10] and the samples investigated by diffuse reflectance laser flash photolysis included Sensitox I and II, the commercially available polymer-bound Rose Bengal sensitizers. Transient absorptions spanning the 600 - 1000 nm region were

detected for both these materials, on excitation at both 354 and 532 nm [11]. Decays of the absorptions were a mixture of first- and second-order processes, with half-lives of 4 μ s and 40 μ s for Sensitox I and Sensitox II respectively. Samples of Rose Bengal adsorbed on polystyrene and polyacrylamide were prepared and similar spectra obtained, and we even succeeded in detecting transient absorptions of cotton fabric dyed with Rose Bengal [11]. The new field opened up by the success of these experiments represents an important step forward in the study of heterogeneous sensitizers and of fabrics of all kinds.

6. Concluding remarks

It is clear that laser flash photolysis has now been successfully extended beyond the transmission mode to include optically dense highly scattering opaque samples in its applications. This extension should bear fruit in the fields of heterogeneous photochemistry, energy transfer in solids etc., and we believe that the technique can now become routine and be of equally useful and important service as is transmission flash photolysis.

Acknowledgments

I thank the Science and Engineering Research Council for the purchase of instrumentation and for support during the period 1981 - 1983 and the University of Technology, Loughborough, for current support. I am indebted to Professor Frank Wilkinson for very valuable and detailed discussions on all aspects of this subject.

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