

## A SENSITIVE OPTICAL GRATING METHOD FOR FLASH PHOTOLYSIS: APPLICATION TO THE CIS-TRANS PHOTOCHEMICAL ISOMERIZATION OF AZO DYES

F. RONDELEZ, H. HERVET and W. URBACH<sup>‡</sup>

*Physique de la Matière Condensée, Collège de France,  
75231 Paris Cedex 05, France*

Received 22 April 1977

Revised manuscript received 20 July 1977

A sensitive optical grating technique has been developed for flash photolysis experiments. The sample is excited by an optical fringe pattern obtained by interfering two light waves derived from a pulsed high power laser. Due to the photochromatic modifications within the sample, a spatially periodic refractive index and/or absorption coefficient distribution is set up, producing a phase and/or amplitude grating respectively. This grating is easily observed through the Bragg diffraction of a second, low intensity, continuous laser beam. The relaxation time of this grating is directly related to the intramolecular relaxation time of the photoexcited states. Preliminary experiments on the cis-trans photoisomerism of an azo dye shows that optical density changes of less than  $10^{-4}$  can be detected, below the limit of resolution with classical transmittance methods.

### 1. Introduction

Flash photolysis is the ideal technique to study the kinetics of photochemical products by the direct measurement of their absorption spectra [1]. The advent of mode-locked lasers has extended the time resolution of the method down to the nanosecond range [2] with little experimental difficulty and even, in some cases, down to the picosecond range [3]. However, progresses are yet to be made to extend the detection sensitivity to small absorption spectra changes. The classical method, which detects the variations of the light intensity transmitted through the sample, is plagued by two severe limitations.

(1) The intensity changes are buried in the average light level of the direct beam, which can be several orders of magnitude higher. Even differential techniques with two carefully matched sample cells cannot detect changes in optical density less than  $10^{-4}$ .

(2) The detection scheme is only sensitive to changes in the optical density of the sample and not

to changes in the optical refractive index.

In this letter, we present an optical grating method derived from laser holography which eliminates these pitfalls. Preliminary experiments on cis-trans photoisomerization are reported for the azo dye methyl red, dissolved in a rigid glass. Using this method, we have been able to detect absorption spectra modifications associated with optical transmission changes of  $10^{-4}$  OD.

The crux of the method is to use a photolytic laser flash with a spatially modulated intensity distribution instead of a uniform one. Since the molecules have different optical properties when photoexcited, an optical grating will be produced in the illuminated sample. This grating will be a phase grating or an amplitude grating depending on which change is dominant at the observation wavelength, either change of the refractive index or of the absorption coefficient respectively [4,5]. In both cases, light incident from a low-intensity monitoring laser beam will be diffracted away from the direct beam into well-defined spots. Observation of the time behavior of the diffracted intensity will yield direct information on the kinetics of the photoexcited molecular states.

<sup>‡</sup> Permanent address: Laboratoire de Biophysique, C.H.U. Cochin, 75014 Paris, France.

## 2. Experimental

Fig. 1 describes our experimental set up. The optical grating is produced by intersecting in the plane of the sample two laser beams issued from a high power argon laser (Spectra Physics model 165, maximum output 880 mW at  $\lambda_1 = 5145 \text{ \AA}$ ). The two beams are of equal intensity, as produced by a beam-splitter—dielectric mirror arrangement and converge onto the sample under an angle  $\Theta$ . In the crossing region, interference effects produce a sinusoidal light intensity pattern with a period  $d \approx \lambda_1/\Theta$ ,  $d$  is adjustable between 10 and  $200 \mu\text{m}$  by varying  $\Theta$ .

Two mechanical choppers give a  $40 \mu\text{s}$  duration to the photolytic light flash with  $2 \mu\text{s}$  transition times and a repetition rate adjustable between 50 Hz and  $5 \times 10^{-3} \text{ Hz}$ . This duration is sufficient to "write" in the sample a photo-induced grating of periodicity  $d$ . The "reading" laser beam (He Ne, 2 mW at  $\lambda_2 = 6328 \text{ \AA}$ , Spectra Physics model 133) is diffracted by this photo-induced grating into well defined spots regularly spaced on a screen in the far field.

The first order diffraction spot is at a distance  $l = (\lambda_1/d)D$  from the direct beam ( $D \approx 1 \text{ m}$  is the distance of the sample to the viewing screen). The time

variation of the diffracted intensity after the photolytic flash is monitored with an XP 2230 Radiotechnique photomultiplier through a  $500 \mu\text{m}$  pin hole. The pin hole ensures that diffracted light is collected over roughly one coherence area [6].

A  $6328 \text{ \AA}$  narrow band interference filter is used to reduce the stray light. The load resistance is  $10 \text{ k}\Omega$  which gives typical analog voltages in the 10 mV range. The signal is finally recorded on a storage oscilloscope or an  $X(t)$  recorder. Commonly, the intensity of the first order diffracted spot amounts to as much as 0.1% of the reading beam light intensity. This corresponds to photon rates  $\approx 6.4 \times 10^{12}$  photons/s, which is enormous if we remember that phototubes can detect single photoelectron events. This makes analog techniques quite sufficient to process the signal. In order to minimize unwanted photochemical processes induced by the monitoring laser beam, its relatively low intensity is further decreased to  $2 \mu\text{W}$  by neutral density filters ( $\text{OD} = 3$ ). For the same reason, its wavelength is chosen away from strong absorption bands of the sample.

Last, the  $\lambda/4$  waveplate is used to convert the polarization of the photolytic laser beam from linear to circular in order to avoid possible polarization-dependent absorbance in dichroic materials as azo dyes [7].

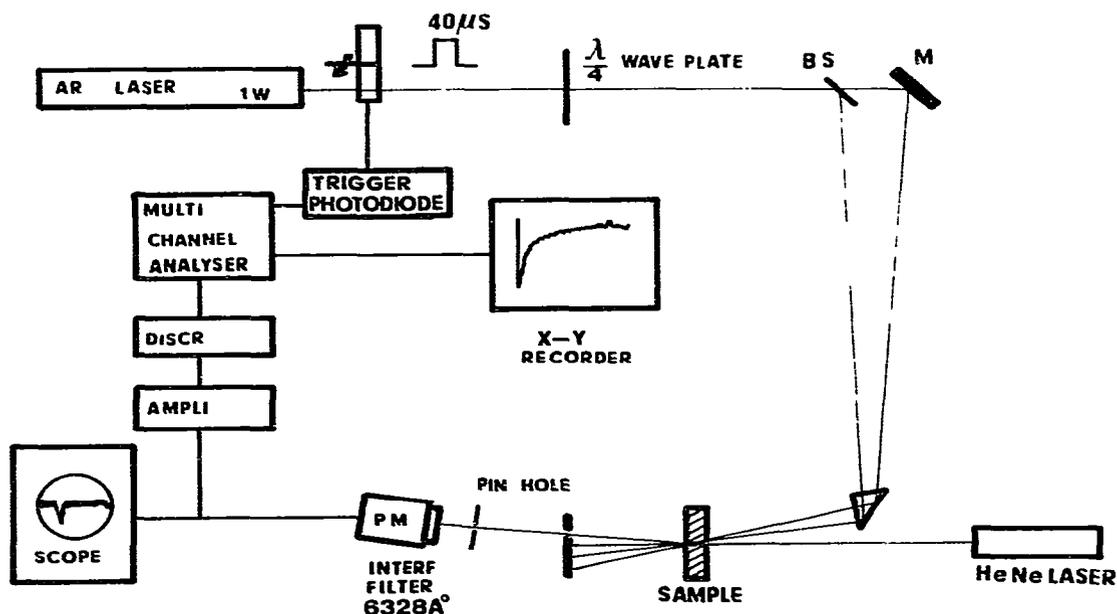


Fig. 1. Experimental set up.

### 3. Results on methyl red dye

The sample used is methyl red, an acid dye of the monoazo series, dissolved into an inert rigid matrix. For the convenience of working at room temperature, we choose Cyanolit 101, a cement of optical quality<sup>†</sup>. Its chemical formula, polycyanomethacrylate (PCMA for short) is very close to the well-known polymethyl methacrylate (PMMA), frequently used as a polar solid solution [8]. PCMA has the advantages over thin film polymeric matrices as PMMA of being solvent free and over epoxy resins [9] of polymerizing spontaneously in humid atmosphere, which avoids high temperature curing.

The concentration of methyl red in PCMA was such that a 200  $\mu\text{m}$  thick sample absorbed 50% to 90% of the incident light intensity at 5145  $\text{\AA}$ .

Fig. 2 shows the time variation of the intensity diffracted into the first-order dot. Immediately after the laser writing flash, the intensity rises to a maximum and then decays back to a steady value. It should be remarked that this last value is noticeably higher than the initial one. As will be shown in the discussion, the observed relaxation corresponds to a single exponential process with a characteristic time of 3.7 s. This value is found to be independent of the grating spacing. Observations at different time scales shows no evidence for faster relaxation processes. On the other hand, we observe no apparent decrease of non-zero value reached after the first relaxation, even on much longer time scales, typically greater than one day.

<sup>†</sup> Cyanolit was obtained from Eleco Products, 92110 Clichy, France.

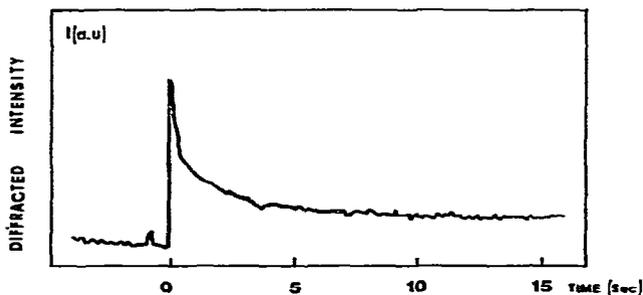


Fig. 2. Time variation of the diffracted intensity after the sample has been illuminated with a single photolytic laser flash (200 mW, 40  $\mu\text{s}$ , 5145  $\text{\AA}$ ); the fringe spacing is 82  $\mu\text{m}$ .

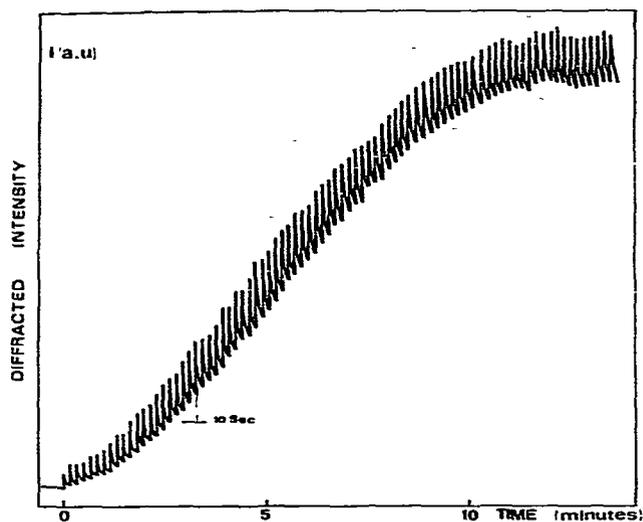


Fig. 3. Time variation of the diffracted intensity when the sample is illuminated with a succession of photolytic laser flashes (200 mW, 40  $\mu\text{s}$ , 5145  $\text{\AA}$ ); repetition rate =  $10^{-1}$  Hz; total duration of the experiment 14 minutes.

When the sample is illuminated with successive laser pulses, the intensity variation is a superposition of spikes on a continuously growing background until saturation is eventually reached (fig. 3). With photolytic laser pulses of 200 mW power and 40  $\mu\text{s}$  duration incident on a 4  $\text{mm}^2$  sample surface, it takes about 80 pulses for the total diffracted intensity to saturate. Visual observation shows that the sample has changed color in the illuminated region, indicating a bleaching.

This saturation can be used to calibrate the experiment and evaluate the sensitivity of the method to small changes in the absorption coefficient. Once the sample is in its fully bleached state, we record its optical absorption spectrum on a standard Varian model 645 spectrophotometer and compare it with the spectrum of an unbleached sample. The two curves, recorded between 6700 and 3200  $\text{\AA}$  are shown in fig. 4. At 6328  $\text{\AA}$  (the reading wavelength) the optical density difference is  $10^{-2}$  (see inset). As this optical density change is typically obtained after 80 pulses, the average change per pulse is of the order of  $10^{-4}$  OD. This small jump in optical density is still clearly detected in the experiment as a single spike. We estimate that the noise in the system is roughly 10 times smaller. This sets the practical detection limit to optical spectra changes associated with absorbance variations of  $10^{-5}$ .

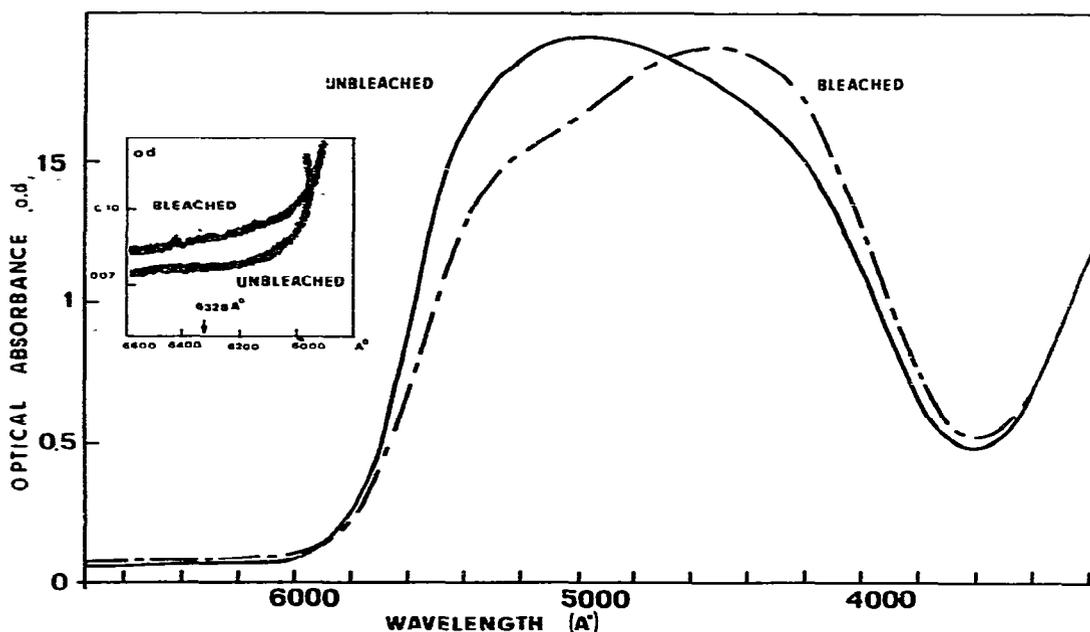


Fig. 4. Absorption spectra of the methyl red sample (a) unbleached; (b) bleached (after the irradiation described in fig. 3). The inset shows a recording at higher sensitivity in the wavelength region of the monitoring laser beam.

However, digital photon counting techniques could further lower this limit.

#### 4. Discussion

It is well known that aromatic azo compounds exhibit cis-trans photoisomerism [10]. The stable trans form is converted by irradiation into the cis form which slowly reverts back in the dark. Azobenzene has been mostly studied but there are also reports on ortho- or para-substituted derivatives [11]. Methyl red is very similar to azobenzene except for an auxochromic carboxyl group in ortho position for one of the benzene rings. This group is responsible for the shift of the strong  $\pi-\pi^*$  transitions into the visible region, which allows us to use the 5145 Å radiation of an argon laser for the photolytic flash.

Since the cis and trans forms are distinct chemical species, with different optical spectra, a photo-induced optical grating will be set up in the sample, due to the spatially periodic flash illumination. This grating will relax through the thermal cis-trans rearrangement. The

relaxation time of  $\approx 2$  s observed in this experiment is typical of the values reported in the literature [11]. As this relaxation process is purely intramolecular, it explains why the time constant is independent of the fringe spacing. If the relaxation of the grating was due to the mass diffusion of photoexcited molecules into non-photoexcited zones and vice versa, the time constant would have shown the usual  $d^2$ -dependence imposed by random walk processes [12]. This diffusion-controlled relaxation process is indeed of importance in liquid solutions and has been observed experimentally [13]. However, in rigid media, mass diffusion is very slow and unobservable in this experiment, even on the longest time scales.

In addition to the reversible cis-trans photoisomerism, we also observe that a permanent photo-induced grating is progressively formed. This could correspond to partial photodecomposition of the methyl red molecules into different molecular species. Their optical spectra in the visible show a maximum in absorption shifted from 5000 Å to 4500 Å. This bleaching is non-reversible over periods of several months.

Regarding the experimental technique, we have al-

ready mentioned that the incident intensity will be diffracted not only by optical absorption changes but also by refractive index changes. Both changes are involved in a photochromic process since the change of absorption  $\Delta\alpha$  is necessarily accompanied by the change of refractive  $\Delta n$  through the Kramers–Kronig relationship. Diffraction theory [14] states that the diffracted intensity is proportional to  $\Delta\alpha^2$  and  $\Delta n^2$  for a pure amplitude or phase grating respectively, in the limit of small peak to peak changes. Unfortunately, in the present case, absolute measurements of  $\Delta\alpha$  and  $\Delta n$  are difficult since there is no simple relationship between the two.

Kinetic measurements are possible however since (1) both  $\Delta\alpha$  and  $\Delta n$  have the same intramolecular relaxation rate; (2) the diffracted intensity  $I_d$  depends on  $\Delta\alpha$  and  $\Delta n$  with the same power law. For simple first order kinetic processes,  $\Delta\alpha$  (or  $\Delta n$ )  $\approx \Delta\alpha_0 \exp(-t/\tau)$  and the diffracted intensity will decrease with a decay time half as great as  $\tau$

$$I_d \approx \Delta\alpha_0^2 \exp(-2t/\tau).$$

In more complicated cases as in the present experiment, where  $\Delta\alpha$  (and/or  $\Delta n$ ) has a non-vanishing part,  $\Delta\alpha_B$ , due to bleaching, the diffracted intensity writes

$$I_d \approx [\Delta\alpha_0 \exp(-t/\tau) + \Delta\alpha_B]^2.$$

The time constant  $\tau$  can still be extracted by taking the square root of  $I_d$  first, then subtracting the background term  $\Delta\alpha_B$  and finally making a semi-log plot versus time. From the data of fig. 2 we get  $\tau \approx 3.7$  s.

The method is highly sensitive. Since the optical grating produced by irradiation in flash photolysis experiments is a combination of an amplitude and of a phase grating, it is reasonable to hope and detect, through the change in refractive index, optical spectra modifications involving absorption changes below the limit of detectability for classical transmittance methods. Refractive index changes of less than  $10^{-7}$ , thermally induced, have already been detected [15,16].

The sensitivity of the optical grating technique is also due to the fact that the conditions for a truly differential measurement are automatically realized, although the method requires only one sample. The light intensity diffracted in the various diffraction orders is only a function of the variations in the optical properties of the photochromic molecules following the flash excitation. No light is diffracted in the

absence of excitation. Thus we do not have to detect small light intensity variations superimposed on a large background. Moreover, the problem of stray light scattered by sample imperfections (solute concentration inhomogeneities, dust particles, scratches on the cell walls) is minimized as this stray light is generally peaked in the forward direction and will not be detected if the diffraction angle imposed by the fringe spacing is large enough. The signal to noise ratio is thus very good.

Finally, we want to emphasize that photolytic experiments on fluid solutions are also possible. We have already mentioned that in this case, the diffracted intensity can decay through a trivial mass-diffusion process. However, it will still be possible to study intramolecular relaxation phenomena as long as the intramolecular relaxation time  $\tau_{\text{intra}}$  is shorter than the diffusion time  $\tau_{\text{diff}}$ . For a given fringe spacing, this sets a limit to the maximum  $\tau_{\text{intra}}$  which can be observed. A fringe spacing of 200  $\mu\text{m}$  corresponds to a diffusion time of 10 s with a diffusion coefficient  $\approx 10^{-6}$   $\text{cm}^2/\text{s}$ , typical of liquids. As this time is large, relaxation by mass diffusion will only be a problem for the very long-lived photochemical processes.

## 5. Conclusion

We have demonstrated that small changes in the optical spectra of photochromic molecules can be detected in flash photolysis experiments by using spatially-modulated light schemes for the laser flash. This optical grating technique has the advantages over the classical transmittance method:

- (1) to be sensitive both to refractive index and absorption coefficient changes;
- (2) to be differential although requiring a single sample cell.

It should be pointed out that absolute measurements of optical properties changes are difficult, kinetic measurements are quite possible.

The method is applicable in rigid media and also in fluid solutions but with some restrictions for the long lived-photoexcited states.

Preliminary experiments on the cis–trans photoisomerization of methyl red show that optical spectra modifications involving absorption changes of less than  $10^{-4}$  OD can be detected.

## References

- [1] N.J. Turro, *Molecular photochemistry* (Benjamin, New York, 1967).
- [2] F. Castelli, *Chem. Phys. Letters* 38 (1976) 528.
- [3] Z.D. Popovic and E.R. Menzel, *Chem. Phys. Letters* 45 (1977) 537, and references therein.
- [4] A.M. Glass, in: *Photonics*, eds. M. Balkanski and P. Lallemand (Gauthier-Villars, Paris, 1975).
- [5] K.S. Pennington, in: *Handbook of lasers*, ed. R.J. Pressley (CRC Press, Ohio, 1971).
- [6] H.Z. Cummins and H.L. Swinney, in: *Progress in optics*, Vol. 8, ed. E. Wolf (North-Holland, Amsterdam, 1970) p. 133.
- [7] G.H. Heilmeyer and L.A. Zanoni, *Appl. Phys. Letters* 13 (1968) 91.
- [8] Z.G. Gardlund, *Polymer Letters* 6 (1968) 57.
- [9] D.L. Ross, *Appl. Opt.* 10 (1971) 571.
- [10] G. Zimmerman, L.Y. Chow and U.J. Paik, *J. Am. Chem. Soc.* 80 (1958) 3258.
- [11] D.L. Ross and J. Blanc, in: *Photochromism, techniques of chemistry* Vol. 3, ed. G.H. Brown (Wiley-Interscience, New York, 1971).
- [12] W. Jost, *Diffusion* (Academic Press, New York, 1960).
- [13] H. Herve, F. Rondelez and W. Urbach, to be published.
- [14] H. Kogelnik, *Bell System Tech. J.* 48 (1969) 2909.
- [15] H. Eichler, G. Salje and H. Stahl, *J. Appl. Phys.* 44 (1973) 5383.
- [16] W. Urbach, H. Herve and F. Rondelez, Presented at the 6th Conference on Liquids Crystals, Kent, Ohio (1976), to be published.