THREE EXPERIMENTS ON TRANSIENT PHOTOCHEMISTRY USING A CW LASER

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The main purpose of this work is the production of photochemical transients with an arbitrary but exactly defined light intensity forcing function $L(t)$. Using a CW laser and electrooptical elements we try to find out under what conditions high power densities will lead to non linear response functions. Up to now we have carried out the following three experiments:

1. $L(t)$ is a step function [1].
   The principle of this method is very simple. Light of a CW laser is focussed on the sample. By means of a Pockels cell it can be turned on or off very rapidly. Luminescence decay times as well as changes in the absorption are measured with a fast photomultiplier. The signal is processed with a fast transient digitizer (Tektronix R 7912). Time resolution for luminescence measurements is limited by the rise time of the Pockels cell. The rise time of our set up is about 5 ns which gives a time resolution of 2 to 3 ns.

2. $L(t) = L_0 \cdot e^{i\omega t}$. (Luminescence decay time with intensity modulated light [1], [2a], [2b].
   A luminescent sample, stimulated with intensity modulated light of appropriate frequency, will emit – linear response provided – intensity modulated light of the same frequency but with a phase shift ϕ_s. By superposing the reference light beam

$$R(t) = R_0 e^{i\omega t} \qquad (1)$$

and the light emitted by the sample

$$S(t) = S_0 e^{i(\omega t + \phi_s)} \qquad (2)$$

on the photomultiplier cathode, we obtain

$$B(t) = R(t) + S(t) = B_0 e^{i(\omega t + \phi)} \qquad (3)$$

The phase shift is given by

$$\phi = \text{arc cos} \frac{B_0^2 - S_0^2 - R_0^2}{2R_0 S_0} \qquad (4)$$

$$\phi = \phi_\ell(\omega) + \phi_s(\omega) = \omega(\Delta t - \frac{\Delta \ell}{c}) \qquad (5)$$

(c = light velocity; $\Delta\ell$ = optical path difference between reference beam and light beam = $\ell_{reference} - \ell_{sample}$; Δt = delay time caused by sample luminescence).

Assuming a single exponential decay, the decay time τ can be calculated by [3]

$$\tau = \frac{1}{\omega} \tan(\Delta t \cdot \omega) \tag{6}$$

The error of τ will only be small if $.5 < \Delta t \cdot \omega < \pi/2$. This condition can always be fulfilled by an appropriate choice of $\Delta \ell$ and ω. As shown in Fig. 1, B_0, R_0, S_0 are measured with a Spectrum Analyzer (Tektronix 7L13). The ratio between the measured signal and the background (coherent RF pick-up) is better than 40 dB. The advantage of an _optical delay line_ is the possibility to check the absolute accuracy of the set-up via length measurement in a very short time, so that artefacts can easily be excluded. Up to now we have obtained an accuracy of ± 50 ps with a modulation frequency of 40 MHz. With some refinements of the optics the time resolution may be improved by at least a factor of two to three.

3. $L(t)$ = constant. (Stationary absorption and emission measurements in a jet stream).
By focussing the light of a commercial rare-gas laser, power densities of 10^6 Watt/cm^2 can easily be obtained. For this reason, high stationary concentrations of excited molecules can be produced, which makes it possible to detect absorption changes (e.g. decrease of the S_0-S_1 absorption, appearance of S_1-S_n or T_1-T_n absorption). The angular dependence of the concentration $N(\theta,t)$ of molecules in the ground state is in the simplest possible case given by

$$\frac{\partial}{\partial t} N(\theta,t) = -J_a(\theta,t) + \frac{1}{\tau}[\frac{N_0}{4\pi} - N(\theta,t)] + D \nabla^2 N(\theta,t) \tag{7}$$

$N(\theta,t) = \frac{Mol}{lt \cdot 4\pi}$; N_0 = total concentration Mol/lt; D = diffusion coefficient; τ = decay time; $\nabla^2 = \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta}$;
$J_a(\theta,t) = \frac{Einstein}{lt \cdot sec \cdot 4\pi}$

$$J_a(\theta,t) = P_0(t) \cdot \frac{\lambda \cdot 3/4\pi \cdot \cos^2\theta}{11,96 \cdot 10^4 \cdot F \cdot \ell} \{1-\exp(-2,3 \cdot \varepsilon \cdot \ell \cdot N(\theta,t))\} \tag{8}$$

$P_0(t)$ = light power (Watt); λ = wave length of the monochromatic laser light (nm); F = irradiated surface (cm^2); ℓ = thickness of the sample (cm); ε = molar extinction coefficient (lt/(Mol·cm)).

To make $(N_0/4\pi - N(\theta,t))$ significantly different from zero for $\theta = 0$, $J_a(\theta,t)$ has to have the magnitude of $1/\tau \cdot N_0/4\pi$. This condition can only be fulfilled if F is very small, because a CW laser has a power $P_0(t)$ of only a few watts. To avoid thermal lensing, a fast flow system must be used for the sample solution. For this reason, we employ the same jet stream as for our CW dye laser [4]. Some typical numbers are: $\tau = 10^{-9}$ sec, $\lambda = 500$ nm, $\ell = 0,03$ cm, $F = 4 \cdot 10^{-6}$ cm^2, $N_0 = 10^{-4}$ mol/lt, $\varepsilon = 5 \cdot 10^4$ lt/(Mol·cm). Resulting $1/\tau \cdot N_0/4\pi = 8 \cdot 10^3$ and $J_a(\theta t) = 2,4 \cdot 10^3 \cdot P_0(t) \cdot \cos^2\theta$.

As an example we have measured in a jet stream the decrease of S_0-S_1-absorption of Rhodamin B using 1 Watt of 5309 Å radiation from a Kr$^+$-laser. These experiments are now being extended and combined with the methods described in 1. and 2.

References:

[1] H. Gugger, S. Leutwyler, E. Schumacher, G. Calzaferri: Kurzzeit-
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[2a] A similar experimental set up has been published by Z.D. Popovic
     and E.R. Menzel: Chem.Phys.Letters 45, 537 (1977).

[2b] An experimental set up with no reference light beam has been published
     by H.P. Haar, U.K.A. Klein, F.W. Hafner and M. Hauser, Chem.Phys.
     Letters 49, 563 (1977).

[3] M. Eigen and L. DeMayer in Techniques of Chemistry, Vol. VI, 1974.

[4] S. Leutwyler, E. Schumacher, L. Wöste, Opt. Communications 19,
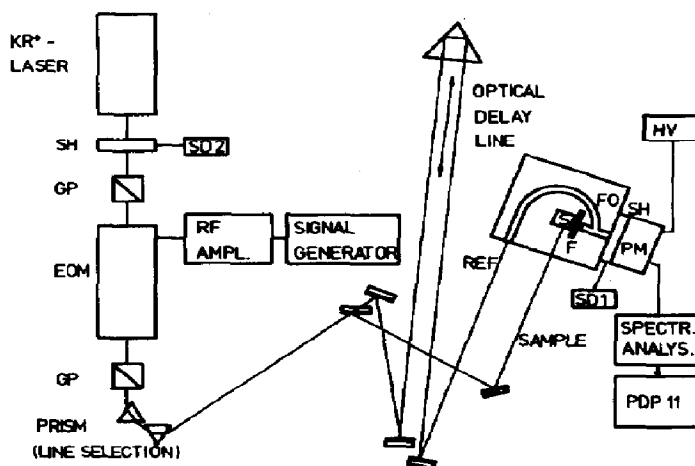   197 (1976).

Figure 1: Experimental set up for luminescence decay time with intensity
           modulated light.
           F = filter, FO = fibre optics, PM = photomultiplier, S = sample,
           SH = shutter, SD1 and SD2 = shutter drivers (coupled),
           GP = glan prism, EOM = electrooptical modulator.