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

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

and the light emitted by the sample

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

on the photomultiplier cathode, we obtain

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

The phase shift is given by

$$\phi = \arccos \frac{B_0^2 - S_0^2 - R_0^2}{2 R_0 S_0} \tag{4}$$

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

$\quad$ (c = light velocity; $\Delta \ell$ = optical path difference between reference beam and light beam = $\ell_{reference} - \ell_{sample}$;
$\quad \Delta t$ = 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 <u>optical delay line</u> 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; $\nabla^2 = \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta}$; $J_a(\theta,t) = \frac{Einstein}{lt \cdot sec \cdot 4\pi}$

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

$P_0(t)$ = 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:

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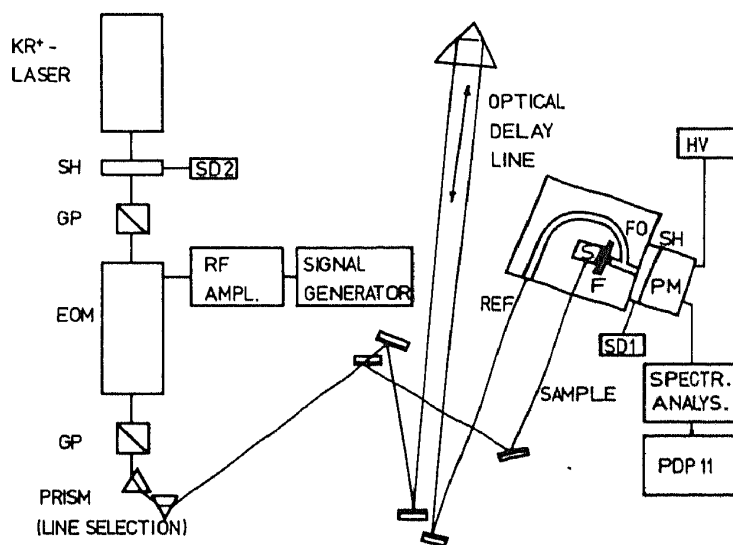   197 (1976).

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.

STUDIES OF THE TEMPERATURE DEPENDENT PHOSPHORESCENCE OF POLY(N-VINYLCARBAZOLE)

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Phosphorescence lifetimes and spectra of solid films of poly(N-vinyl-carbazole) (PVCA) have been examined over the temperature range from 77°K - 298°K. At 77°K the usual phosphorescence emissions at 490 nm and 518 nm are observed but the intensity of the higher energy emission is much more temperature sensitive than the lower so that only the 518 nm signal remains at 298°K. The activation energies for radiative decay of these two signals are 0.6 kcal/mole (490 nm) and 2.9 kcalmole (518 nm). If, as has been previously supposed, these two emissions are from trapped triplet species, then these energies represent the respective trap depths. An unexpected result is that the mobile triplet energy level in solid PVCA is calculated to be about 20,500 cm^{-1} from these results whereas the N-alkyl carbazolyl chromophore has a lowest triplet energy of about 23,000 cm^{-1}.

The solid films of PVCA are cast from solution using either benzene or methylene chloride as solvent. Usually the films are air-dried but unmistakable increases in delayed luminescence intensity are observed after heating an air-dried film overnight in a vacuum oven. Although delayed luminescence from PVCA films has been detected up to about 175°K, the spectra obtained in this study are apparently the first examples of room temperature delayed luminescence from this polymer. Air-dried films from methylene chloride or films cast from either solvent and then vacuum dried give easily detected spectra at room temperature. Since neither benzene nor methylene chloride have quantum states accessible from the mobile PVCA triplet, it is concluded that the residual solvent molecules disrupt the formation of trap sites in the polymer leading to decreased intensities of phosphorescence and delayed fluorescence.