Picosecond Phenomena II, Springer Series in Chem. Phys. 14, Eds. R.M. Hochstrasser et al (1980)

Measurement of Excited State Absorption Cross Sections in Dye Solutions with Picosecond Light Pulses

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1. Introduction

In excited state absorption measurements intense pump pulses promote molecules to excited states and weak probe beams induce transitions to higher lying states. The measurement of absolute excited state absorption cross-sections is complicated by the fact that the transmission of probe light depends on the number of excited molecules, on their orientational distribution and on the angle between the involved transition moments.

In the past several techniques have been developed for the measurement of absolute excited singlet state absorption cross-sections: i) orientation free absorption spectra were measured with pump and probe beam polarizations oriented under an angle of 54.7° [1]; ii) the excited state absorption was investigated after complete bleaching of the ground state [2]; and iii) the absorption measurements were compared with numerical simulations [3].

Here a further technique is described which avoids the problems of orientational anisotrppy: An intense picosecond pump pulse (frequency ν_P) populates the S_1-state. After molecular reorientation (delay time $t_D \approx 2\tau_{or}$) two probe beams are applied. One probe pulse at frequency ν_P measures the excited population and the other probe beam at frequency ν_L monitors the excited state absorption.

The method is applied to determine the absolute excited state absorption cross-sections $\sigma_e(\nu_L)$ of rhodamine 6G and rhodamine B in ethanol for a transition between the singlet states S_1 and S_4.

2. Description

In Fig.1 a simplified level scheme of the rhodamine dyes is presented. A pump pulse of frequency ν_P = 18.960 cm^{-1} (second harmonic of a modelocked Nd-glass laser; duration Δt_P = 5 ps) promotes the molecules to the S_1-band. Excited state absorption

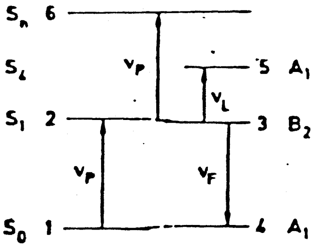

Fig.1 Energy level diagram for rhodamine dyes.

at frequency ν_P leads to transitions to level 6. A probe beam of frequency ν_L = 9 480 cm^{-1} excites molecules from the S_1 to the S_4 level. This state is frequently termed as S_2 when two weakly absorbing lower lying singlet states [4] are neglected.

After reorientation of the excited molecules in the S_1-state the transmission of the probe beam at frequency ν_L is given by

$$T_e = \exp\,[-\sigma_e(\nu_L)\int_0^\ell N_3(z)dz] \qquad (1)$$

$\sigma_e(\nu_L)$ is the isotropic S_1-S_4 excited state absorption cross-section at frequency ν_L.

The total population $\int_0^\ell N_3(z)dz$ of level 3 is monitored with the probe beam of frequency ν_P. Its transmission through the sample is

$$T = \exp\,\{-\sigma_{12}\,N\ell + [\sigma_{12} - \sigma_e(\nu_P)]\int_0^\ell N_3(z)dz\} \qquad (2)$$

$N = N_1(z) + N_3(z)$ is the total number density of dye molecules in the solution. σ_{12} and $\sigma_e(\nu_P)$ are the isotropic ground state and excited state absorption cross-sections at frequency ν_P. ℓ is the sample length.

Solving Eq. 2 for $\int_0^\ell N_3(z)dz$ and inserting the result into Eq. 1 leads to

$$\sigma_e(\nu_L) = \frac{\ln(T_e)[\sigma_e(\nu_P)-\sigma_{12}]}{\ln(T) + \sigma_{12}\,N\ell} \qquad (3)$$

Eq. 3 is valid when: i) the excited state population $N_3(r)$ is constant over the cross-sections of the probe beams, ii) the stimulated emission cross-section $\sigma_{em}(\nu_L)$ at frequency ν_L is negligibly small. iii) the transfer to triplet states may be neglected, iv) the probe beams do not affect the level populations (weak probe beam powers), and v) an isotropic orientational distribution in the S_1 state is established (delay of probe beams $t_D = 2\tau_{or}$).

3. Experiment

The experimental setup is depicted in Fig.2. A modelocked Nd-glass laser is used. A single pulse is selected with an electro-optical shutter and increased in energy with a Nd-glass amplifier. The second harmonic pump pulse is generated in a KDP crystal. A BK7 glass block is used for temporal separation of the fundamental and second harmonic pulses. The transmitted laser pulses at ν_P and ν_L are reduced in intensity and reflected back to the sample. They act as time delayed probe pulses and their transmissions are measured with detectors PD1-4.

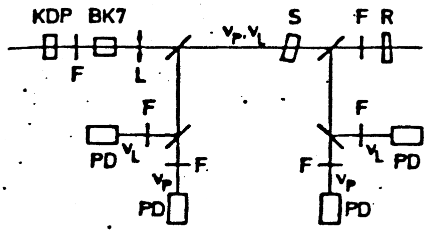

Fig. 2 Experimental arrangement. KDP, crystal for second harmonic generation; F, filters; BK7, glass block (length 10 cm) for temporal separations of probe beams ν_P and ν_L; S, dye sample; R, reflecting glass wedge; PD, photodetectors.

4. Results

The parameters of the analysed dyes [5] together with the determined excited state absorption cross-sections $\sigma_e(\nu_L)$ are listed in Table 1. The $\sigma_e(\nu_L)$-values are rather small. In case of rhodamine 6G, $\sigma_e(\nu_L)$ should be approximately equal to the peak S_1-S_4 absorption cross-section (transition to a position slightly above the S_4 potential energy curve [6]). The peak S_0-S_4 absorption in rhodamine 6G is a factor of two larger than the S_1-S_4 absorption ($\sigma(S_0\text{-}S_4) = 4.5\times10^{-17}$ cm^2 at $\nu = 28600$ cm^{-1}). Our results agree with Dolan and Goldschmidt [2] who found $\sigma(S_1\text{-}S_4) \approx 1.5\times10^{-17}$ cm^2 for rhodamine 6G.

The measurement of absolute excited state absorption cross-sections at fixed frequencies allows the calibration of qualitative excited state absorption spectra which may be obtained with picosecond light continua [7].

Table 1

	Rhodamine 6G	Rhodamine B
concentration	1.65×10^{-5} M	2.9×10^{-5} M
solvent	ethanol	ethanol
σ_{12}	4.17×10^{-16} cm^2	2.1×10^{-16} cm^2
$\sigma_e(\nu_P)$	5×10^{-17} cm^2	5×10^{-17} cm^2
$\sigma_e(\nu_L)$	$(2 \pm 0.2)\times10^{-17}$ cm^2	$(4 \pm 1)\times10^{-18}$ cm^2

References

1. H.E. Lessing and A. von Jena, Chem. Phys. Lett. 59, 249 (1978).
2. G. Dolan and C.R. Goldschmidt, Chem. Phys. Lett. 39, 320 (1976).
3. A. Müller, J. Schulz-Hennig and H. Tashiro, Appl. Phys. 12, 333 (1977).
4. H. Jacobi and H. Kuhn, Z. Elektrochem. 66, 46 (1962).
5. W. Falkenstein, A. Penzkofer and W. Kaiser, Opt. Comm. 27, 151 (1978).
6. C. Orner and M.R. Topp, Chem. Phys. Lett. 36, 295 (1975).
7. A. Penzkofer and W. Kaiser, Opt. Quant. Electr. 9, 315 (1977).