Excited-State Absorption Cross-Sections in Rhodamine Dyes Determined after Molecular Reorientation (*).

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Summary. — A method is described to measure absolute excited-state absorption cross-sections of dye molecules in solution. The problems of orientational anisotropy are avoided by probing the population and absorption of the excited state after molecular reorientation. Excited-state absorption cross-sections are measured for rhodamine 6 G and rhodamine B at a fixed frequency of 9480 cm^{-1}.

1. – Introduction.

Excited-state absorption spectroscopy with picosecond light pulses provides new information on energy levels and on the dynamics of transitions [1-3]. Intense pump pulses populate an excited state and weak probe beams induce transitions to higher-lying states. The measurement of absolute excited-state absorption cross-sections is aggravated by the fact that the absorption of probe light depends on the number of excited molecules, on their orientational distribution and on the angle between the involved transition moments.

Several absorption spectroscopic methods have been developed to take care of these difficulties: i) the problems of orientational anisotropy are avoided for pure electronic dipole transitions when linearly polarized pump

(1) A. MÜLLER, J. SCHULZ-HENNIG and H. TASHIRO: *Appl. Phys.*, **12**, 333 (1977).
(2) B. I. GREENE, R. M. HOCHSTRASSER and R. B. WEISMAN: *J. Chem. Phys.*, **70**, 1247 (1979).
(3) J. JARAUDIAS, P. GAUJON and J. C. MIALOQ: *Chem. Phys. Lett.*, **45**, 107 (1977).

and probe beams with polarizations under a well-defined angle of $\psi = 54.7°$ (tg^2 $\psi = 2$) are used ([4]); ii) specially oriented elliptical beams also produce rotation-free absorption spectra ([5]); iii) intense pump pulses bleach the ground state nearly completely and almost all molecules are in the excited state which approaches an isotropic orientational distribution ([6,7]); iv) the absorption is measured for a given experimental situation and a numerical simulation extracts the excited-state absorption cross-section ([1]).

In this paper we describe a further technique for the measurement of excited-state absorption cross-sections. This method determines the excited-state population and circumvents the orientational problems. It is independent of the nature of the absorption processes for ground-state and excited-state absorption. The molecules are excited with a picosecond pump pulse and they rearrange to an isotropic distribution (reorientation time τ_{or}). After reorientation, two weak probe pulses are applied (delay time $t_D \simeq 2\tau_{or}$). One probe beam measures the excited-state population and the other probe beam monitors the excited-state absorption. The technique is used to determine the excited-state absorption cross-sections $\sigma_e(\tilde{\nu}_L = 9480\ \text{cm}^{-1})$ for rhodamine 6G and rhodamine B dissolved in ethanol at room temperature. The involved transition starts from the S_1-state and ends in a higher singlet state S_4 which absorbs around 350 nm in conventional absorption spectroscopy. This state is often termed as S_2-level ([8-11]) when two weakly absorbing lower-lying singlet states ([12-14]) are neglected.

2. – Description.

The structural formulae of the investigated molecules rhodamine 6G and rhodamine B are shown in fig. 1. The conventional ground-state absorption spectrum of rhodamine 6G dissolved in ethanol is depicted in fig. 2 together with positions of the singlet states S_1 to S_7 and oscillator strengths for dipole transitions between S_0 and the higher singlet states. These energy levels and oscillator strengths were obtained by Pariser-Parr-Pople (PPP) calculations

([4])   H. E. LESSING and A. VON JENA: *Chem. Phys. Lett.*, **59**, 249 (1978).
([5])   H. E. LESSING and A. VON JENA: *Chem. Phys. Lett.*, **42**, 213 (1976).
([6])   G. DOLAN and C. R. GOLDSCHMIDT: *Chem. Phys. Lett.*, **39**, 320 (1976).
([7])   A. V. ARISTOV and V. S. SHEVANDIN: *Opt. Spectrosc. USSR*, **43**, 131 (1977).
([8])   S. MORY, D. LEUPOLD and R. KÖNIG: *Opt. Commun.*, **6**, 394 (1972).
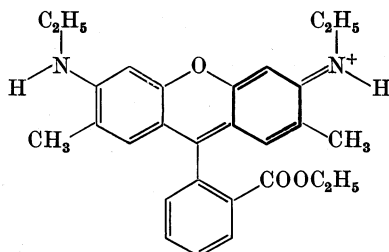([9])   G. C. ORNER and M. R. TOPP: *Chem. Phys. Lett.*, **36**, 295 (1975).
([10])   J. P. HERMANN and J. DUCUING: *Opt. Commun.*, **6**, 101 (1972).
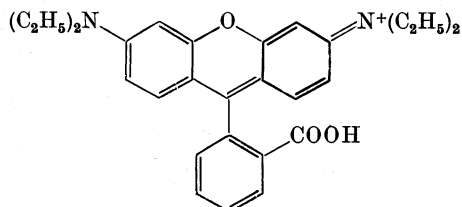([11])   V. L. BOGDANOV, V. P. KLOCHKOV and B. S. NEPORENT: *Opt. Spectros. USSR*, **43**, 701 (1977).
([12])   H. JAKOBI and H. KUHN: *Z. Elektrochem.*, **66**, 46 (1962).
([13])   A. V. ARISTOV and V. S. SHEVANDIN: *Opt. Spectrosc. USSR*, **44**, 276 (1978).
([14])   A. V. ARISTOV and V. S. SHEVANDIN: *Opt. Spectrosc. USSR*, **45**, 825 (1978).
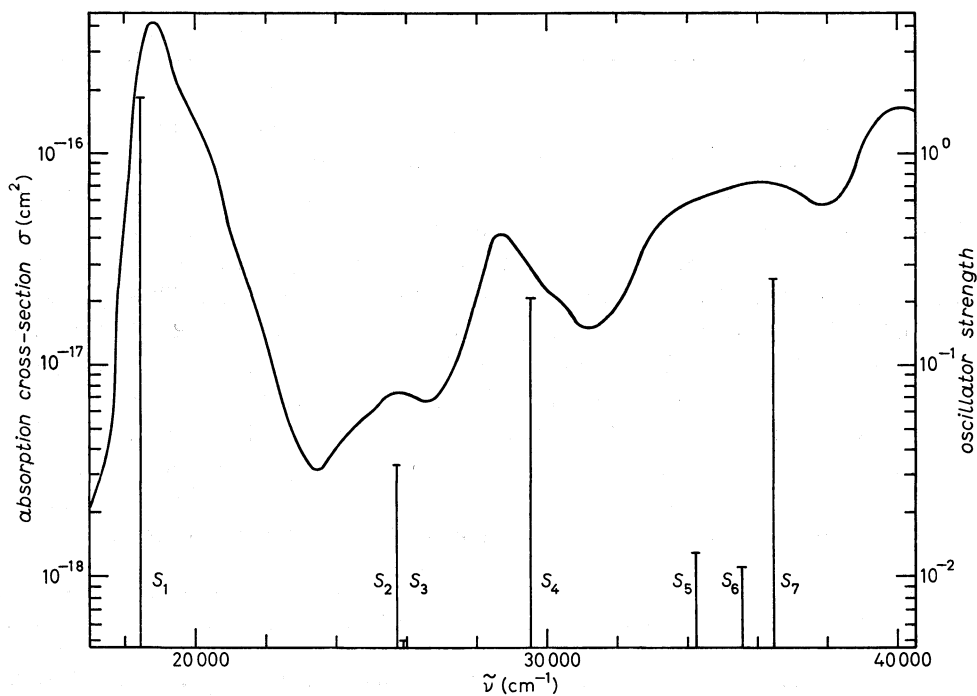
Rhodamine 6G.
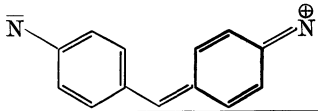
Rhodamine B.

Fig. 1. – Structural formulae of rhodamine 6G and rhodamine B.

Fig. 2. – Ground-state absorption spectrum of rhodamine 6G in ethanol and oscillator strengths for S_0-S_i ($i = 1$ to 7) transitions (from PPP calculations).

with a computer program of Greenwood ([15]). The molecular skeleton and the parameters used in the calculations are presented in table I.

TABLE I. – *Parameters for PPP calculations on rhodamine dyes.*

molecular skeleton	
number of conjugated atoms	$N = 15$
number of doubly occupied orbitals	$M = 8$
effective nuclear charges	$Z_C = 1, \quad Z_N = 2$
core integrals	$\omega_C = -11 \text{ eV}, \quad \omega_N = -26 \text{ eV}$
resonance integrals	$\beta_{CC} = \beta_{CN} = -2.37 \text{ eV}$
electron repulsion integrals	$\gamma_{\mu\mu}(C) = 11.35 \text{ eV}$
	$\gamma_{\mu\mu}(N) = 14.09 \text{ eV}$
	$\gamma_{\mu\nu}(C\!-\!C) =$

$$= \gamma_{\mu\nu}(C\!-\!N) = \begin{cases} 14.4 \text{ eV}/D & (D > 2.81 \text{ Å}), \\ 4.97 \text{ eV} & (2.81 \text{ Å} \geqslant D > 2.75 \text{ Å}), \\ 5.77 \text{ eV} & (2.75 \text{ Å} \geqslant D > 1.42 \text{ Å}), \\ 7.19 \text{ eV} & (1.42 \text{ Å} \geqslant D) \end{cases}$$

(D is the atomic distance).

The level scheme of fig. 3 is reduced to the states involved in our experiments ([16,17]). An intense picosecond pump pulse of frequency ν_P promotes molecules from the ground state 1 (S_0) to the Franck-Condon state 2 in the S_1-band. The excited molecules relax with a time constant $\tau_{23} \simeq 1$ ps to the equilibrium position 3 in the S_1-singlet state ([18]). The molecules return to the ground state by radiative (rate k_{34}) and radiationless (rate k_{31}) transitions. The quantum efficiency for fluorescence emission (frequency ν_F) is $\eta = k_{34}/k_3 \simeq 0.88$ for rhodamine 6G and 0.5 for rhodamine B. The intersystem crossing rate k_{3T} (singlet-triplet transfer) is negligibly small ($k_{3T}/k_3 \simeq 2 \cdot 10^{-3}$ for rhodamine 6G and $5 \cdot 10^{-3}$ for rhodamine B). The spontaneous-emission lifetimes for rhodamine 6G and rhodamine B are $\tau_F = 1/k_3 = 1/(k_{31} + k_{34} + k_{3T}) \simeq 4.2$ ns and 2.7 ns, respectively ([16]). Excited-state absorption of the pump pulse and the fluorescence light occurs from level 3 to region 6 ([6,7,18,19]). The molecules in region

([15]) H. H. GREENWOOD: *Computing Methods in Quantum Organic Chemistry* (London, 1972).

([16]) W. FALKENSTEIN, A. PENZKOFER and W. KAISER: *Opt. Commun.*, **27**, 151 (1978).

([17]) A. PENZKOFER and W. FALKENSTEIN: *Opt. Quant. Electr.*, **10**, 399 (1978).

([18]) A. PENZKOFER, W. FALKENSTEIN and W. KAISER: *Chem. Phys. Lett.*, **44**, 82 (1976).

([19]) A. V. ARISTOV and V. S. SHEVANDIN: *Opt. Spectrosc. USSR*, **42**, 111 (1977).
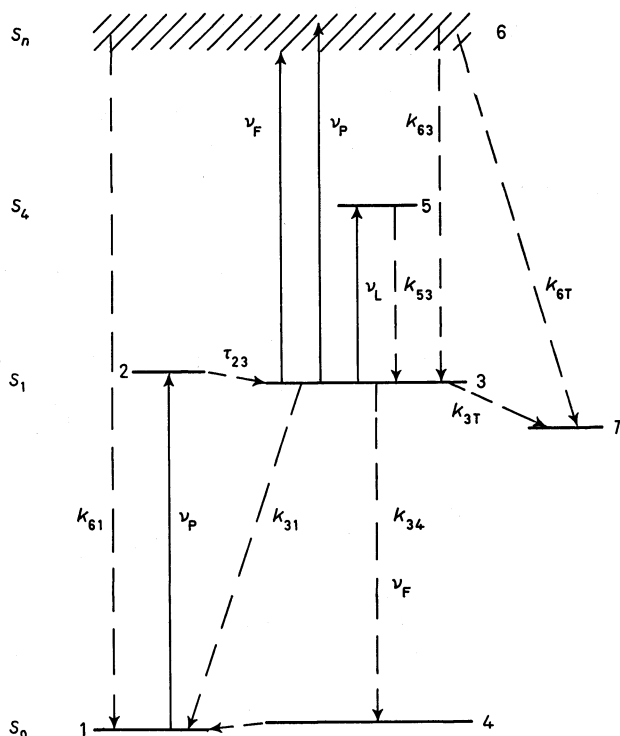
Fig. 3. – Schematic level system for excited-state absorption in rhodamine dyes.

6 relax within $1/k_6 = 1/(k_{61} + k_{63} + k_{6r}) \lesssim 0.1$ ps ([16,20,21]). They decay mainly to the S_1-singlet state ($k_{63}/k_6 \simeq 0.95$ for rhodamine 6G and 0.7 for rhodamine B). The transfer to triplet and decomposition states is of the order of 0.01 ([16]). The molecules in level 3 reorient with a time constant $\tau_{or} \simeq 270$ ps (solvent ethanol, room temperature) ([22-24]). The excited-state transition from level 3 to level 5 is induced with probe light of frequency ν_L.

At a delay time of $t_D \simeq 2\tau_{or}$, two weak picosecond probe beams of frequency ν_P and ν_L are passed through the dye sample to determine the (orientation averaged) excited-state absorption cross-section $\sigma_e(\nu_L)$. The transmission of probe beam 1 (frequency ν_L) through the sample (length l) is

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

([20]) C. V. SHANK, E. P. IPPEN and O. TESCHKE: *Chem. Phys. Lett.*, **45**, 291 (1977).
([21]) I. KAPLAN and J. JORTNER: *J. Chem. Phys.*, **32**, 381 (1978).
([22]) T. J. CHUANG and K. B. EISENTHAL: *Chem. Phys. Lett.*, **11**, 368 (1971).
([23]) P. J. SADKOWSKI and G. R. FLEMING: *Chem. Phys. Lett.*, **57**, 526 (1978).
([24]) H. E. LESSING and A. VON JENA: in *Laser Handbook*, Vol. **3**, edited by M. L. STITCH (Amsterdam, 1979), p. 753.

The total population $\int_0^l N_3(z)\,\mathrm{d}z$ is monitored with probe beam 2 of frequency ν_P. Its transmission through the sample is

$$(2) \qquad T = \exp\left[-\sigma_{12}\int_0^l N_1(z)\mathrm{d}z - \sigma_e(\nu_P)\int_0^l N_3(z)\,\mathrm{d}z\right] =$$

$$= \exp\left[-\sigma_{12}Nl + [\sigma_{12} - \sigma_e(\nu_P)]\int_0^l N_3(z)\,\mathrm{d}z\right].$$

$N = N_1(z) + N_3(z)$ 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 (values determined in ([16,18])). A rearrangement of eq. (2) leads to

$$(3) \qquad \int_0^l N_3(z)\,\mathrm{d}z = \frac{\ln T + \sigma_{12}Nl}{\sigma_{12} - \sigma_e(\nu_P)}.$$

Insertion of eq. (3) into eq. (1) gives the isotropic excited-state absorption cross-section at frequency ν_L

$$(4) \qquad \sigma_e(\nu_L) = \frac{\ln(T_e)[\sigma_e(\nu_P) - \sigma_{12}]}{\ln T + \sigma_{12}Nl}.$$

In the derivation of eq. (4) the following approximations are made:

i) A uniform excited-state population $N_3(r)$ is assumed over the cross-sections of the probe beams.

ii) Equation (1) more completely reads $T_e = \exp\left[-[\sigma_e(\nu_L) - \sigma_{em}(\nu_L)]\cdot \int_0^l N_3(z)\,\mathrm{d}z\right]$ and the left-hand side of eq. (4) should be replaced by $\sigma_e(\nu_L) - \sigma_{em}(\nu_L)$. The stimulated-emission cross-section $\sigma_{em}(\nu_L)$ for fluorescence emission from S_1 to S_0 at frequency ν_L is neglected in our case, since it is very small $\left(\sigma_{em}(\nu_L) \leqslant 10^{-18}\ \mathrm{cm^2}\ ([8])\right)$.

iii) The small loss of molecules in the singlet system due to transfer to triplet and decomposition states is neglected ([16,17]). It amounts to about 1 % under our experimental conditions (see k_{3T}/k_3 and k_{6T}/k_6 values cited above and eq. (31) of ([17])).

iv) The probe beams should not affect the level populations. The intensity of probe beam 1 (frequency ν_L) is not critical, since the saturation intensity $I_s \simeq h\nu_L k_{53}/\sigma_e(\nu_L)$ for bleaching of level 3 is of the order of $10^{11}\ \mathrm{W/cm^2}$ $\left(k_{53} \simeq 10^{13}\ \mathrm{s^{-1}}\ ([13,21,25]),\ \sigma_e(\nu_L)\ \text{values see below}\right)$. In our experiments a probe beam

([25]) M. D. GALANIN and S. A. TSCHISCHKOWA: *Kratk. Soobshch. Fiz.*, **4**, 35 (1971).

peak intensity of $I_0(\nu_L) \simeq 5 \cdot 10^8$ W/cm^2 is used. The probe beam 2 of frequency ν_P monitors the population of the ground state and its photon density $n(\nu_P) = \int_{-\infty}^{\infty} I(\nu_P)\,\mathrm{d}t/h\nu_P$ (photons/cm^2) has to be small compared to the density of molecules Nl (molecules/cm^2). In our experiments it is $n(\nu_P) \simeq 0.1\, Nl$ $\left(I_0(\nu_P) \simeq 10^8\ \text{W/cm}^2\right)$. The excited-state population $\int_0^l N_3(z)\,\mathrm{d}z$ (eq. (3)) is overestimated by about 10 % and the $\sigma_e(\nu_L)$ values of eq. (4) have to be increased by about 10 %. These corrections have been carried out for the $\sigma_e(\nu_L)$ data reported below. Smaller photon densities $n(\nu_P)$ of probe beam 2 may be applied with more sensitive photodetectors.

v) An isotropic orientational distribution of excited molecules is assumed at a delay time of $t_D \simeq 2\tau_{or}$. In fig. 4 the orientational distribution
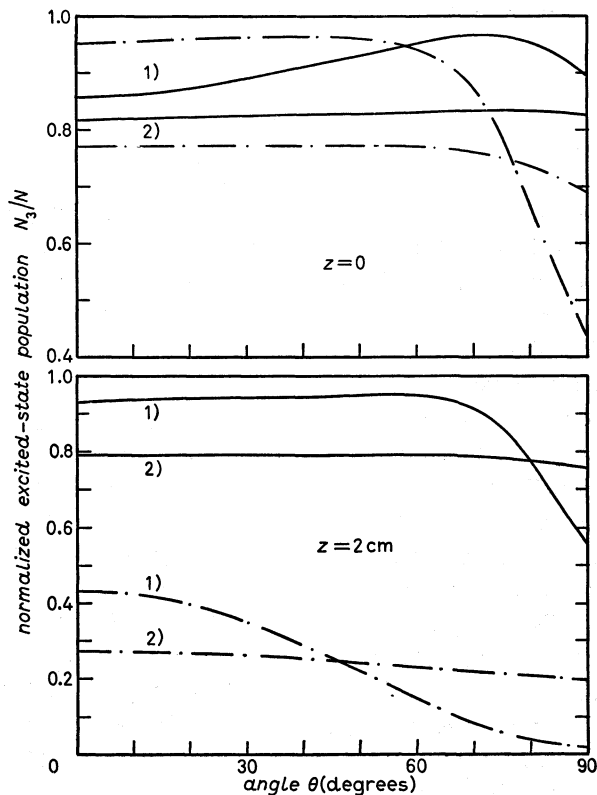

Fig. 4. – Orientational distribution of the S_1-state of rhodamine 6G at the entrance and the end of the sample for $t_D = 15$ ps (curves 1)) and 540 ps (curves 2)) after excitation. Pump pulse parameters: peak intensities $I_{OP} = 5 \cdot 10^9$ W/cm^2 (solid curves) and $I_{OP} = 10^9$ W/cm^2 (dashed curves), duration $\Delta t_P = 5$ ps (FWHM), shape Gaussian. Dye parameters: concentration $1.65 \cdot 10^{-5}$ M ($N = 10^{16}$ cm^3), solvent ethanol, $\tau_{or} = 270$ ps, $\tau_F = 4.2$ ns.

$N_3(\theta)$ is calculated for rhodamine 6G ($1.65 \cdot 10^{-5}$ M in ethanol) at times $t_D = = 3\Delta t_P = 15$ ps and $t_D = 2\tau_{or} = 540$ ps ($t_D = 0$ at the peak of the pump pulse). Curves are shown for $I_{OP} = 10^9$ W/cm^2 and $5 \cdot 10^9$ W/cm^2 at the entrance ($z = 0$) and at the end of the sample ($z = l = 2$ cm). The equation system of ref. ([17]) was used in the calculations (eq. (5) of ([17]) was extended to include the molecular reorientation). θ is the angle between the electrical-field strength of the pump pulse and the transition dipole moment for ground-state absorption. At $t_D = 15$ ps the excited-state population is anisotropic: For peak intensities $I_{OP} > 10^9$ W/cm^2 the population $N_3(\theta)$ is reduced at small angles θ due to excited-state absorption of the pump pulse and incomplete returnal of molecules from higher excited states to level 3. For large angles θ the population $N_3(\theta)$ reduces due to the small absorption cross-section in this range $\left(\sigma_{12}(\theta) = 3\sigma_{12} \cos^2 \theta \,(^{4,18}) \right)$. At intensities $I_{OP} < 10^9$ W/cm^2 the excited-state population $N_3(\theta)$ decreases gradually with increasing θ. The curves calculated for $t_D = 540$ ps show a rather flat distribution of $N_3(\theta)$ throughout the sample length.

3. – Experiment.

The experimental set-up for the excited-state absorption studies is shown in fig. 5. A mode-locked Nd-phosphate glass laser ($\tilde{\nu}_L = 9480$ cm^{-1}) is used for the measurements ([26]). A single pulse is selected with an electro-optical switch and its energy is increased with a Nd-phosphate glass amplifier. The light pulse behind the amplifier has a duration of $\Delta t_L \simeq 6$ ps, a band width of $\Delta \nu_L \simeq 3$ cm^{-1} and an energy of about 5 mJ. The second harmonic of the laser light is generated in a KDP crystal (length 1 cm, conversion efficiency 0.3) and it is used as pump pulse ($\tilde{\nu}_P = 18\,960$ cm^{-1}). The fundamental laser pulse is reduced in intensity with filter F1 and acts as probe beam 1. A glass block (BK7, length 10 cm) separates the fundamental and second-harmonic light pulses by about 10 ps to avoid coherent grating effects ([27,28]). The lens L ($f = 800$ mm) increases the peak intensity of the pump pulse at the sample cell S up to $5 \cdot 10^9$ W/cm^2 (beam diameter at the sample $\simeq 2$ mm). The pump pulse transmission through the sample is limited to $\leqslant 0.3$ for rhodamine 6G and $\leqslant 0.1$ for rhodamine B due to excited-state absorption. The transmitted light signals at frequencies ν_L and ν_P are reduced in intensity by filter F6 and are reflected back to the sample with a wedged glass plate R. They act as probe beams 1 and 2. The distance between sample and reflector provides the time delay between pump and probe pulses. For rhodamine 6G a distance of 9 cm

([26]) A. LAUBEREAU and W. KAISER: *Opto-electronics*, **6**, 1 (1974).
([27]) C. V. SHANK and D. M. AUSTON: *Phys. Rev. Lett.*, **34**, 479 (1975).
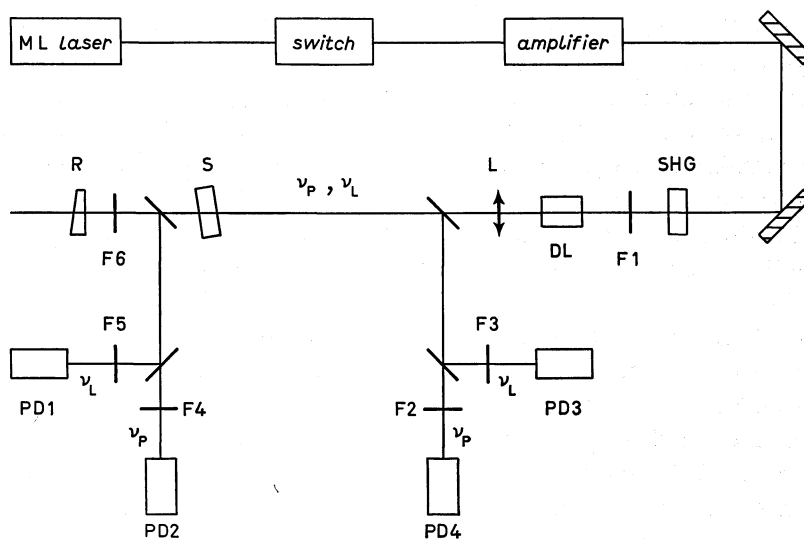([28]) H. J. EICHLER: *Opt. Acta*, **24**, 631 (1977).

Fig. 5. – Experimental set-up. SHG, KDP crystal for second-harmonic generation. F1-F6, filters. DL, glass block for temporal separation of light pulses at ν_P and ν_L. L, lens ($f = 800$ mm). R, glass plate for reflection of probe beams. PD1-4, vacuum photocells. S, dye sample (length 2 cm).

was used ($t_D \simeq 600$ ps). In the case of rhodamine B the distance was reduced to 6 cm ($t_D \simeq 400$ ps) because of the shorter fluorescence lifetime. The sample is near the focus of the reflected probe beams. The excited-state population N_3 is approximately constant over the beam diameter of the probe beams (≈ 0.5 mm). The detectors PD1 and PD3 measure the transmission T_e, while the detectors PD2 and PD4 determine T.

4. – Results.

The parameters of the analysed dyes which enter eq. (4) are summarized in table II together with the determined isotropic excited-state absorption cross-sections $\sigma_e(\nu_L)$. The dye concentrations were small to avoid problems

TABLE II.

Dye	Rhodamine 6G	Rhodamine B
solvent	ethanol	ethanol
concentration	$1.65 \cdot 10^{-5}$ M	$2.9 \cdot 10^{-5}$ M
σ_{12}	$4.17 \cdot 10^{-16}$ cm²	$2.1 \cdot 10^{-16}$ cm²
$\sigma_e(\nu_P)$	$5 \quad \cdot 10^{-17}$ cm²	$5 \quad \cdot 10^{-17}$ cm²
$\sigma_e(\nu_L)$	$(2 \pm 0.2) \cdot 10^{-17}$ cm²	$(4 \pm 1) \cdot 10^{-18}$ cm²

of dimerization and kation-anion spectral shifts (for rhodamine B) ([23,29]). The low dye concentrations hinder efficient amplified spontaneous emission which decreases the lifetime of the S_1-state ([16,17]). At $I_{OP} = 5 \cdot 10^9$ W/cm² excited-state transmissions of $T_e = 0.75$ and 0.91 are measured for rhodamine 6G and rhodamine B, respectively. The $\sigma_e(\nu_L)$ values in the table were obtained by averaging over about hundred shots. It should be noted that the small excited-state absorption cross-section of $\sigma_e(\nu_L) = 4 \cdot 10^{-18}$ cm² in case of rhodamine B could be measured, which demonstrates the sensitivity of the applied method.

The S_1-S_4 excited-state absorption should be compared with the S_0-S_4 ground-state absorption. In rhodamine 6G the S_1-S_4 Franck-Condon transition from level 3 to 5 ends about 200 cm⁻¹ above the S_4 potential-energy curve ([9]), so that the measured $\sigma_e(\nu_L)$ value of $2 \cdot 10^{-17}$ cm² should be approximately equal to the peak S_1-S_4 absorption cross-section. The peak S_0-S_4 ground-state absorption cross-section of rhodamine 6G is $4.5 \cdot 10^{-17}$ cm² ([30]) ($\tilde{\nu} = 28\,600$ cm⁻¹). In the case of rhodamine B the S_1-S_4 transition at frequency ν_L ends approximately 300 cm⁻¹ below the S_4 potential curve and the peak S_1-S_4 absorption cross-section should be larger than the measured value of $\sigma_e(\nu_L) = 4 \cdot 10^{-18}$ cm². The peak S_0-S_4 absorption cross-section of rhodamine B is $3.5 \cdot 10^{-17}$ cm² ($\tilde{\nu} = 28\,300$ cm⁻¹). In ref. ([8]) a $\sigma(S_1$-$S_4)$ value for rhodamine 6G was estimated from laser threshold measurements which is a factor of 6 larger than our value. A cross-section of $\sigma(S_1$-$S_4) \simeq 1.5 \cdot 10^{-17}$ cm² for rhodamine 6G was reported in ref. ([6]) by absorption of xenon light after bleaching of ground-state absorption by the second harmonic of a Q-switched Nd-glass laser.

5. – Conclusions.

The described technique for the measurement of excited-state absorption cross-sections is applicable to systems with reorientation times τ_{or} shorter than fluorescence lifetimes and weak intersystem crossing rates. 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 ([31]).

<p align="center">* * *</p>

([29]) J. FERGUSON and A. W. H. MAU: *Chem. Phys. Lett.*, **17**, 543 (1972).
([30]) K. H. DREXHAGE: in *Topics of Applied Physics*, Vol. **1**, edited by F. P. SCHÄFER (Berlin, 1977), p. 144.
([31]) A. PENZKOFER and W. KAISER: *Opt. Quant. Electr.*, **9**, 315 (1977).

● RIASSUNTO (*)

Si descrive un metodo per misurare le sezioni d'urto assolute di assorbimento dello stato eccitato di molecole di coloranti in soluzione. I problemi di anisotropia orientazionale sono evitati sondando l'occupazione e l'assorbimento dello stato eccitato dopo riorientamento molecolare. Le sezioni d'urto d'assorbimento dello stato eccitato sono misurate per la rodamina 6G e la rodamina B con frequenza fissa a 9480 cm^{-1}.

(*) *Traduzione a cura della Redazione.*

Поперечные сечения поглощения на возбужденных состояниях в красителях родамина, определенные с помощью переориентации молекул.

Резюме (*). — Описывается метод измерения абсолютных поперечных сечений поглощения на возбужденных состояниях молекул красителя в растворе. Проблемы, связанные с опиентационной анизотропией, удается обойти посредством исследования заселенности возбужденного состояния и поглощения возбужденным состоянием после переориентации молекул. При фиксированной частоте 9480 см$^{-1}$ измеряются поперечные сечения поглощения на возбужденных состояниях родамина 6 G и родамина B.

(*) *Переведено редакцией.*