MEASUREMENT OF ABSORPTION CROSS SECTIONS IN THE LONG-WAVELENGTH REGION OF THE $S_0-S_1$ ABSORPTION BAND OF DYES

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In the long-wavelength region of the $S_0-S_1$ absorption band of dyes only a fraction of molecules takes part in the absorption process. The absorption cross section of the molecules involved is deduced from non-linear transmission measurements with picosecond light pulses. The absorption cross sections $\sigma_A(\nu_L)$ (\nu_L\ is the ruby-laser frequency) of 1,1'-diethyl-2,4'-carbocyanine iodide in methanol and oxazine 1 perchlorate in ethanol are determined.

1. Introduction

All dye molecules contribute to the $S_0-S_1$ absorption spectrum around the absorption peak and at the short-wavelength side. The absorption cross section $\sigma_A$ is easily derived from transmission measurements with a spectrophotometer ($\sigma_A = \alpha_A / N_0$, $\alpha_A = -\ln(T_0) / l$, where $\alpha_A$ is the absorption coefficient, $N_0$ the total number density of dye molecules, $T_0$ the small signal transmission and $l$ the sample length). In the long-wavelength region of the $S_0-S_1$ absorption band only a fraction of molecules takes part in the absorption process (thermally excited molecules and inhomogeneously shifted molecules) and the absorption cross section of the molecules involved can no longer be determined with a spectrophotometer.

The absorption cross section in this long-wavelength region ($\nu < \nu_{F,m}$; $\nu_{F,m}$ is the frequency of peak fluorescence emission) is generally derived from fluorescence measurements [1–3]. Here a non-linear transmission technique with picosecond light pulses is described for the measurement of the absorption cross sections. The technique is applied to measure the absorption cross section $\sigma_A(\nu_L)$ of two dyes, dicyanine (1,1'-diethyl-2,4'-carbocyanine iodide, DCI') [4–6] in methanol and oxazine 1 perchlorate [7,8] in ethanol, at the ruby-laser frequency $\nu_L$. The results of the bleaching technique are compared with the results of the fluorescence technique.

The non-linear transmission technique with picosecond pulses as it is described in the following is limited to dyes with negligible singlet–triplet absorption cross sections and with intersystem-crossing rates small compared to the inverse picosecond pulse duration. Furthermore the dyes should completely dissolve to monomers.

2. Theory

Fig. 1a shows a singlet potential-energy diagram of a dye molecule. The transitions of peak $S_0-S_1$ absorption at $\nu_{A,m}$, of peak $S_1-S_0$ emission at $\nu_{F,m}$ and the most probable transition of laser light at $\nu_L$ ($\nu_L < \nu_{F,m}$) are indicated. The rovibrational levels of the ground state are thermally populated. The $S_0-S_1$ frequency spacing is inhomogeneously broadened. A multitude of transitions between $S_0$ and $S_1$ rovibrational levels are possible at a fixed laser frequency.

Fig. 1b indicates the absorption and emission cross sections. The apparent absorption cross section $\bar{\sigma}_A(\nu) = \alpha_A(\nu) / N_0$ and apparent emission cross section $\bar{\sigma}_E(\nu) = \alpha_E(\nu) / N_0$ (\alpha_E is the stimulated emission coefficient) are given by the solid curves [3,9]. The absorption cross section of really inter-
inhomogeneously broadened molecules overcomes with approximately equal strength. For sorption and stimulated emission cross sections (solid curves) approximately the same stimulated emission cross state have anomalously relaxed molecules in the S becomes equal to the apparent stimulated emission molecules in the long-wavelength tail Fm 0 S band to the S relaxed band. Therefore, the S moiety in the S band are identical band and can take part in the absorption process. reduces because only a tail of thermally excited and inhomogeneously shifted molecules in the absorption region, \( \tilde{\sigma}_E(\nu) \) follows exactly the theory of ref. [3] where the possible S 0–S 1 transitions are comprised in a two-level system (levels 1 and 2 of fig. 1a, for details see ref. [3]). \( \sigma_A(\nu_L) \) is obtained by comparing experimental energy-transmission data with calculated energy-transmission curves \( T_E(I_{0L}, \Delta t_L) \). The initial condition for the interacting molecules is \( N_i(\theta, r, r', -\infty, \alpha) = \sigma_A(\nu_L)/ \sigma_A(\nu_L) = -\ln(T_0)/\sigma_A(\nu_L) \) which involves the parameter \( \sigma_A(\nu_L) \) to be determined. The energy transmission depends on the pulse parameters \( I_{0L} \) (peak intensity), \( s(r', t') \) (temporal and spatial pulse shape, gaussian shape used in calculations), \( \Delta t_L \) (pulse duration) and on the dye parameters \( \sigma_A(\nu_L) \), \( \tau_F \) (fluorescence lifetime), \( T_3 \) (spectral cross-relaxation time), \( \sigma_{ex} \) (excited-state absorption cross section), \( \tau_{ex} \) (relaxation time of levels populated by excited-state absorption) and \( \tau_{or} \) (reorientation time of transition dipole moments).

The pulse parameters are measured in the ex-
Experiments. The dye parameters $\sigma_A(v_L)$ and $\sigma_{ex}(v_L)$ are determined from the energy-transmission measurements. $\sigma_{ex}(v_L)$ is obtained by fitting the calculated energy-transmission curves at high input intensities to the energy-transmission data. It is given by

$$\sigma_{ex}(v_L) = -\kappa \ln[T_E(I_{0L} \to \infty)] \sigma_A(v_L)/\sigma_A(v_L),$$

with $\kappa$ close to one [3]. It should be small compared to $\sigma_A(v_L)$. For $\sigma_{ex}(v_L)$ comparable to $\sigma_A(v_L)$ the described picosecond bleaching technique cannot be used. The $S_1$-state lifetime $\tau_F$ has to be measured separately, for example by streak camera measurements of the fluorescence decay after picosecond pulse excitation or by absorption-recovery analysis with picosecond pump and probe techniques (methods reviewed in refs. [9,11,12]).

The spectral cross-relaxation time $T_3$ describes refilling of depopulated levels in the $S_0$ band by thermalisation and redistribution within the inhomogeneous profile [3]. For $T_3 \gg \Delta t_L$ no refilling of states in the interaction region of the $S_0$ band occurs. Complete bleaching is observed when half of the initially present molecules is transferred to the $S_1$ state. The level populations at complete bleaching are $N_1 = N_2 = \frac{1}{2} N_i(t' = -\infty)$. In the case of $T_3 \ll \Delta t_L$ the involved states in the $S_n$-band are refilled from the $S_0$ reservoir and complete bleaching is observed for the level populations $N_i(t' = -\infty)$. A pulse energy of a factor of two higher is necessary for $T_3 \ll \Delta t_L$ compared to $T_3 \gg \Delta t_L$ in order to achieve the same bleaching effect. In our calculations we assumed $T_3 \ll \Delta t_L$. The reported $\sigma_L$ values would be a factor of two smaller for $T_3 \gg \Delta t_L$. The $S_n$ state populated by excited-state absorption is assumed to relax to the $S_1$ state with a decay time $\tau_{ex}$ which is generally in the subpicosecond region [13-15]. $\tau_{ex} = 10^{-13}$ s is used in the calculations. In some dye molecules $S_2$-state lifetimes in the picosecond [16-22] and sub-nanosecond-to-nanosecond region [23,24] have been found. The slight influence of $\tau_{ex}$ on $\sigma_L$ determination is discussed below.

3. Experiments

The absorption cross sections of the dyes dicyanine in methanol and oxazine 1 in ethanol have been measured. For the fluorescence technique [eqs. (1)-(3)] the $S_0-S_1$ absorption spectra were measured with a conventional spectrophotometer [$\bar{\sigma}_A(\nu)$] and the fluorescence spectral shapes $E(\nu)$ were obtained by He–Ne-laser excitation and fluorescence detection at right angles to the excitation beam with a spectrometer and an optical multichannel analyser.

The bleaching technique was performed with single picosecond pulses from a mode-locked ruby laser. The energy transmission through the dyes was measured with photodetectors. The input-pulse peak intensity was determined by two-photon transmission measurements through a CdS crystal [25] (the error in the single-shot peak-intensity detection is $\pm 10\%$). The ruby-laser pulse duration was determined by two-photon fluorescence detection [26].

4. Results

The $S_0-S_1$ absorption spectra $\bar{\sigma}_A(\nu)$ and the fluorescence spectra $\bar{\sigma}_F(\nu)$ of solutions of dicyanine in methanol and oxazine 1 in ethanol are shown in figs. 2 and 3, respectively. The absorption cross sections at the ruby-laser frequency are $\sigma_A(v_L) = \bar{\sigma}_A(v_L) = (3.1 \pm 0.3) \times 10^{-16}$ cm$^2$ for dicyanine and $(2.5 \pm 0.3) \times 10^{-16}$ cm$^2$ for oxazine 1.

The energy-transmission data are depicted in

![Fig. 2. Absorption and fluorescence spectrum of dicyanine (DCI') in methanol.](image-url)
values to the experimental points, $\sigma_A$ (dicyanine) = $(3 \pm 0.4) \times 10^{-16}$ cm$^2$ and $\sigma_A$ (oxazine 1) = $(2.2 \pm 0.4) \times 10^{-16}$ cm$^2$, are included in Table 1. Each data point represents an average over about ten shots. The error bars indicate the standard deviation. The influence of the $S_2-S_1$ decay time $\tau_{ex}$ on the measurement of the long-wavelength absorption cross section was analysed for the dyes studied. The influence is found to be small. For example, if $\tau_{ex} = 10$ ps is assumed instead of $\tau_{ex} = 0.1$ ps the best-fitting $\sigma_A$ and $\sigma_{ex}$ values change by less than 10% to $\sigma_A$ (dicyanine) = $3.0 \times 10^{-16}$ cm$^2$, $\sigma_{ex}$ (dicyanine) = $9.1 \times 10^{-17}$ cm$^2$, $\sigma_A$ (oxazine 1) = $2.4 \times 10^{-16}$ cm$^2$ and $\sigma_{ex}$ (oxazine 1) = $2.2 \times 10^{-17}$ cm$^2$.

The $\sigma_{ex}(v_L)$ data determined by fluorescence techniques [8] and by the bleaching technique agree quite well.

In the case of dicyanine $\tau_F \ll \Delta t_L$ and the energy transmission is strongly intensity dependent [9,27]. For oxazine 1 we have $\tau_F \gg \Delta t_L$ so that the energy transmission is determined by the pulse energy [9,28]. In both cases the measurement of $T_L(I_{0L}, \Delta t_L)$ allows the determination of the long-wavelength absorption cross section $\sigma_A$.

Table 1  
Parameters used and results

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<th>Parameter</th>
<th>Dicyanine</th>
<th>Oxazine 1</th>
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<td>1020 b)</td>
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<td>$\sigma_A(p_L)$</td>
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<tr>
<td>$\Delta t_L$ (ps)</td>
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</table>

a) Ref. [6].  b) Ref. [8].  c) Assumed.  d) Ref. [29].

e) Estimated from the Debye–Stokes–Einstein hydrodynamic model [30].

f) This work.
5. Conclusions

A picosecond pulse bleaching technique has been described for the measurement of the absorption cross section of molecules absorbing at the long-wavelength side of the $S_0$-$S_1$ absorption band. The technique is applicable if the excited-state absorption $\sigma_{ex}$ is smaller than the absorption cross section $\sigma_A$ and the $S_1$-state lifetime is known from other measurements. The excited-state absorption cross section and the ground-state absorption cross section are determined. The method is applicable independent of the duration of the $S_1$-state lifetime compared to the picosecond pump pulse duration.

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References