

Transient excited singlet state absorption in Rhodamine 6G*

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Abstract. Transient excited singlet state absorption (ESSA) has been studied in Rhodamine 6G in ethanol using a nitrogen laser and nitrogen laser-pumped dye laser. Broad absorption with several submaxima and possible shoulders, which represent the vibrational structure, has been observed in Rhodamine 6G in the region, 4175-4640 Å. The position of the lowest vibrational level of the first excited singlet state S_1 has been determined from the crossing point of the long and short wavelength spectral wings of absorption and fluorescence respectively. The energy level scheme of the molecule has been obtained with the help of the absorption and fluorescence spectra recorded. The observed structure in ESSA has been tentatively interpreted to be due to transitions from the different vibrational levels of S_1 to one or more vibrational levels of the upper singlet electronic state S_4 .

Keywords. Rhodamine 6G; excited singlet state absorption; absorption spectra; fluorescence spectra.

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1. Introduction

Laser dyes like Rhodamine 6G are a class of organic molecules which show lasing action under appropriate conditions of excitation. Dye lasers are among the most useful types of lasers because of their easy tunability, wavelength coverage and simplicity (Schafer 1983; Pavlopoulos and Hammond 1974; Sorokin *et al* 1967; Sorokin *et al* 1968; Shank 1975; Peterson 1979). Dyes can be used in solid, liquid or gaseous phase and their concentration and hence their absorption and gain can be readily controlled. Solutions of dyes are especially convenient for experimental studies. Different scintillators, coumarins, xanthenes, oxazines and polymethines can be conveniently chosen to cover a wide range of the spectrum from 3200 Å to 13000 Å.

The ground electronic state of a dye molecule is in general a singlet state (Schafer 1983). The first excited singlet state is generally higher than the lowest triplet state. Dye molecules, when excited to the higher singlet states, relax by nonradiative interactions to the lowest excited singlet state S_1 in a short time of the order of picoseconds. This is the only state from which dye molecules have been observed to fluoresce, which, in most cases, have lifetimes of a few nanoseconds. Also this is the state from which the radiative transition that is directly responsible for laser action takes place under appropriate conditions of stimulation in all laser dye molecules.

Though singlet to triplet state inter-system transitions are generally forbidden, relaxation of molecules in the S_1 to the lowest triplet state T_1 is possible through

induced processes. This singlet $S_1 \rightarrow$ triplet T_1 decay will decrease the net available excited singlet state population for stimulated emission thus affecting the lasing efficiency of dyes, particularly in the CW mode of operation.

The other process which affects the lasing efficiency of dyes is the excited singlet state absorption (ESSA). As the state S_1 has a radiative lifetime which is longer than the non-radiative relaxation times of the higher excited singlet electronic states, dye molecules in the S_1 state can undergo absorptive transitions in addition to stimulated emissive transitions in the presence of a pump beam.

The study of these two processes is of great interest because of the widespread use of laser dyes. However, the present study concerns itself with the excited singlet state absorption which may be called transient absorption as the lifetime of the first excited singlet state is of the order of few nanoseconds.

Sahar and Wieder (1973) obtained excited singlet state absorption of Acridine Red in ethanol in the region, 20000–25000 cm^{-1} with a maximum at about 22800 cm^{-1} using nitrogen laser coupled with a tunable dye laser. Sahar and Wieder (1974) also reported cross-sections for excited state absorption of some of the laser dyes at the nitrogen laser wavelength of 3371 Å. Shah and Leheny (1974) and Leheny and Shah (1975) obtained ESSA in Cresyl violet perchlorate in methanol in the region, 2–2.9 eV with a maximum at 2.45 eV. These experiments demonstrated the influence of the excited state absorption at the pump wavelength on the pumping efficiency and at the probe laser wavelength on the gain per pass. Dolan and Goldschmidt (1976) reported absolute cross-section measurements on the ESSA of Rhodamine 6G in ethanol. They reported ESSA in the region, 2700–4650 Å with a maximum at 4400 Å and a sub-maximum at about 3950 Å. Sahar and Treves (1977) studied ESSA of a few dyes like Rhodamine 6G and Rhodamine B in ethanol using dual beam laser photolysis experiment in the nanosecond range. They reported excited state absorption with maxima at about 5300 Å and 5650 Å in Rhodamine 6G. Nitrogen laser and nitrogen laser-pumped dye laser were used in these studies.

In all the above experiments, transient ESSA spectra were observed to consist of broad maxima and the transitions involved were not identified except in Rhodamine 6G in which Sahar and Treves suggested that the ESSA obtained by them was due to $S_1 \rightarrow S_3$ transition.

The study of ESSA in Rhodamine 6G, α -NPO, POPOP and dimethyl POPOP has been undertaken recently in this laboratory. The spectra show broad absorption with a coarse structure consisting of a number of submaxima and shoulders.

As a comprehensive energy level scheme essential for the analysis of the observed ESSA is not available for any of these dyes in literature, absorption and fluorescence spectra of these molecules have been recorded as part of this work. The analysis of the absorption and fluorescence spectra yielded the energy level schemes needed and the excited singlet state absorption in each of the four dyes is sought to be analyzed on the basis of these energy level schemes. This paper deals with the results obtained in Rhodamine 6G in solution.

2. Experimental details

2.1 Absorption and fluorescence spectra

Absorption spectrum of Rhodamine 6G in ethanol has been recorded using Perkin-Elmer model 323 UV-Vis-NIR spectrophotometer in the region, 2000–7000 Å. The dye

was obtained from Kodak and was used without further purification. Also its fluorescence spectra excited by a mercury lamp and a nitrogen laser (3371 Å) have been recorded using the same spectrophotometer.

The laser source of fluorescence was a 1 MW pulsed nitrogen laser system (Moletron model UV24) with a pulse width of 8 nsec and a variable pulse repetition rate of 1–100 pps. Fluorescence from the dye cell was collected in a direction normal to that of the nitrogen laser beam and focussed on to the entrance slit of the spectrophotometer. The light output from the spectrophotometer was detected by a photomultiplier tube (Hamamatsu R928). The output signal current, after being amplified by a current amplifier (Keithley model 427), was fed to a boxcar integrator (EG&G PAR model 162) for signal processing and to an oscilloscope (Tektronix model 2465) for visual monitoring. The boxcar integrator and the oscilloscope were triggered by a synchronous trigger pulse from the nitrogen laser operated at 20 pps. The aperture delay of the integrator was so chosen as to permit the sampling of the current pulse at its peak. The aperture duration and the time constant of the integrator were so adjusted as to obtain optimum signal-to-noise ratio consistent with the spectral scan rate. The output of the boxcar integrator was recorded on the strip chart recorder.

2.2 Excited singlet state absorption

The experimental arrangement for recording the ESSA is shown in figure 1. The output of the 1 MW nitrogen laser (NL) was split into two beams of unequal intensity (75:25) using a beam splitter (BS). The stronger of these two beams was steered to pass through the dye solution in the absorption cell (AC) which results in populating the S_1 state as almost every absorbed photon will produce a molecule in that state. The absorption by the molecules in the S_1 state was probed by another beam obtained by pumping a dye laser with the other beam having 25% intensity of the nitrogen laser output. The dye laser beam was directed by using a suitable optical arrangement to cross the excited dye volume normal to the direction of the pump beam. An optical delay line (ODL) was used to adjust the delay between the pump and the probe pulses to an optimum value (~ 3 nsec). Since most of the pump beam gets absorbed within the first few millimeters of the dye solution, the probe beam was made to pass through the

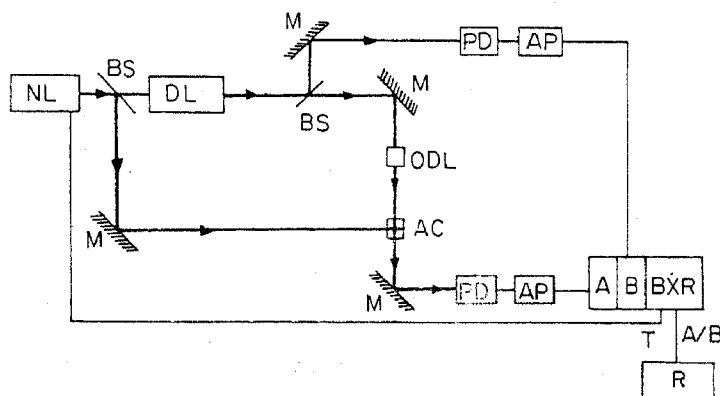


Figure 1. Schematic diagram of the experimental arrangement to study the excited singlet state absorption. AC, absorption cell; AP, amplifier; BS, beam splitter; BXR, box-car integrator; DL, dye laser; M, mirror; NL, nitrogen laser; ODL, optical delay line; PD, photodiode detector; R, strip-chart recorder.

absorption cell close to its wall on which the pump beam was incident so as to ensure maximum possible interaction with the excited state population. To make the pumping more effective the pump beam was focussed on the dye solution in the absorption cell using a quartz cylindrical lens. The probe beam, after passing through the highest intensity region of the pump beam in the absorption cell, was detected by a photodetector (PD UDT model 10DP) and the signal, after being amplified by an amplifier (AP) was processed using a boxcar integrator (BXR). The detected signal A was normalized with respect to the input of the probe beam to take into account any possible fluctuations in the intensity of the probe beam. A second beam splitter (BS) reflected 4% of the input beam which was detected by another photodetector (PD) and the output B of this detector was used for normalization. The normalized output A/B from the boxcar integrator was recorded on a strip chart recorder.

In the experiment, initially, the absorption cell was filled with pure solvent and the transmission curve was recorded by scanning the dye laser through the region of interest. The absorption cell was then filled with the dye solution and the experiment was repeated to obtain absorption, if any, due to the molecules in the ground state S_0 . Next, the nitrogen laser beam was turned on so as to allow it to excite the molecules in the ground state to populate the first excited singlet state S_1 and the transmission curve was recorded to obtain the absorption due to the molecules in the S_1 state as well as the absorption, if any, due to the molecules in the S_0 state. This absorption was greater than that obtained in the absence of the pump beam.

The excited singlet state absorption extends over a considerable region of the spectrum. Since the tuning range of the dye laser with a single laser dye does not cover the whole region of interest, three different dyes have been used. These are Stilbene 420(4180–4300 Å), Coumarin 440(4250–4500 Å) and Coumarin 1(4430–4780 Å).

3. Results

3.1 Rhodamine 6G

3.1a Absorption and fluorescence: The absorption spectrum of Rhodamine 6G in ethanol (figure 2) shows maxima at (18605, 18810, 20140)*, 28660, (33840, 36220)*, 40420, 44730 and 49490 cm^{-1} . The strong absorption in the visible region extends from 17295–22725 cm^{-1} and shows a peak at 18810 cm^{-1} accompanied by two shoulders at 20140 and 18605 cm^{-1} . Assuming that the maxima appearing alone or in close lying groups in the absorption spectrum correspond to the vertical energies of excitation from the lowest vibrational level of the ground state S_0 to one or more vibrational levels of the different upper singlet electronic states, the energy levels labeled S_1, S_2, S_3, S_4 etc of Rhodamine 6G shown in figure 3, were arrived at.

The fluorescence spectra of this dye molecule excited by the mercury lamp (3125.7, 3650.2, 4046.6, 4358.4 and 5460.7 Å) and by the nitrogen laser (3370 Å) have been found to be identical. This suggests that regardless of the state to which they are initially excited, the dye molecules relax through fast nonradiative transitions to the lowest excited singlet electronic state S_1 , where thermalization is established in a time much

* The wave numbers shown in parantheses correspond to a group of maxima or submaxima or shoulders lying close enough to one another to be considered as arising from a single electronic transition.

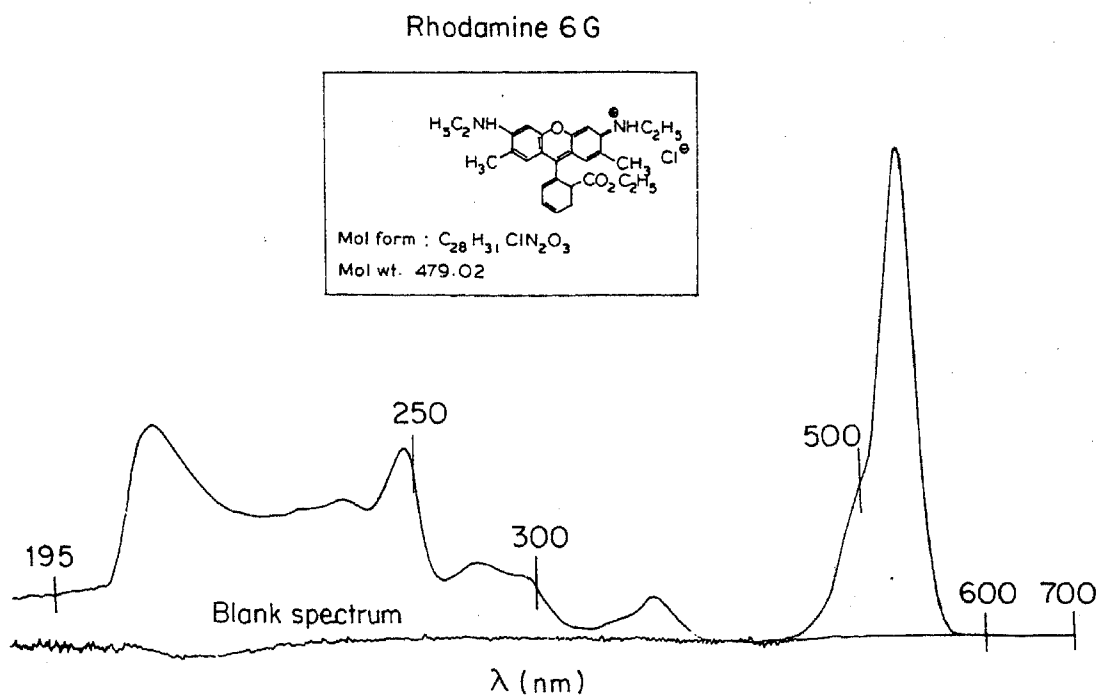


Figure 2. Absorption spectrum of Rhodamine 6G in ethanol.

shorter than the radiative lifetime of that state. The fluorescence spectrum in solution extends from $14425\text{--}18755\text{ cm}^{-1}$ with a maximum at 17635 cm^{-1} and a shoulder at 16710 cm^{-1} .

The fluorescence spectrum rises steeply on its short wavelength side while the absorption spectrum falls steeply on its long wavelength side. The short-wavelength edge of fluorescence is at 18755 cm^{-1} while the long-wavelength edge of absorption is at 17295 cm^{-1} . The normalized fluorescence $Q(\lambda)/Q_{\max}$ and the normalized absorption $\epsilon(\lambda)/\epsilon_{\max}$ spectral wings in the region, $17295\text{--}18755\text{ cm}^{-1}$ have been plotted in figure 4. They appear to be mirror images of each other resulting from a reflection in a plane passing through the point of intersection of these spectra, as is to be expected in the case of any dye molecule.

The point of intersection which is found to be 18110 cm^{-1} , represents the position of the lowest vibrational level of the excited singlet state S_1 above that of the ground state S_0 (Schafer 1983). This is shown accordingly in figure 3. Assuming that the fluorescence maximum at 17635 cm^{-1} and the shoulder at 16710 cm^{-1} arise as a result of transitions from the lowest vibrational level of the S_1 state at 18110 cm^{-1} to two different vibrational levels of the ground state, one obtains the levels at 475 and 1400 cm^{-1} shown in figure 3.

3.1b Excited singlet state absorption: The excited singlet state absorption of Rhodamine 6G in ethanol was recorded in the region $4175\text{--}4640\text{ \AA}$ as described earlier. If I_0 is the incident intensity of the probe beam I the transmitted intensity through the solvent and I_2 and I_1 are respectively the transmitted probe beam intensities with and without the pump beam, then

$$I = I_0 \exp(-\alpha)L,$$

$$I_1 = I_0 \exp(-(\alpha + \sigma_g N)L)$$

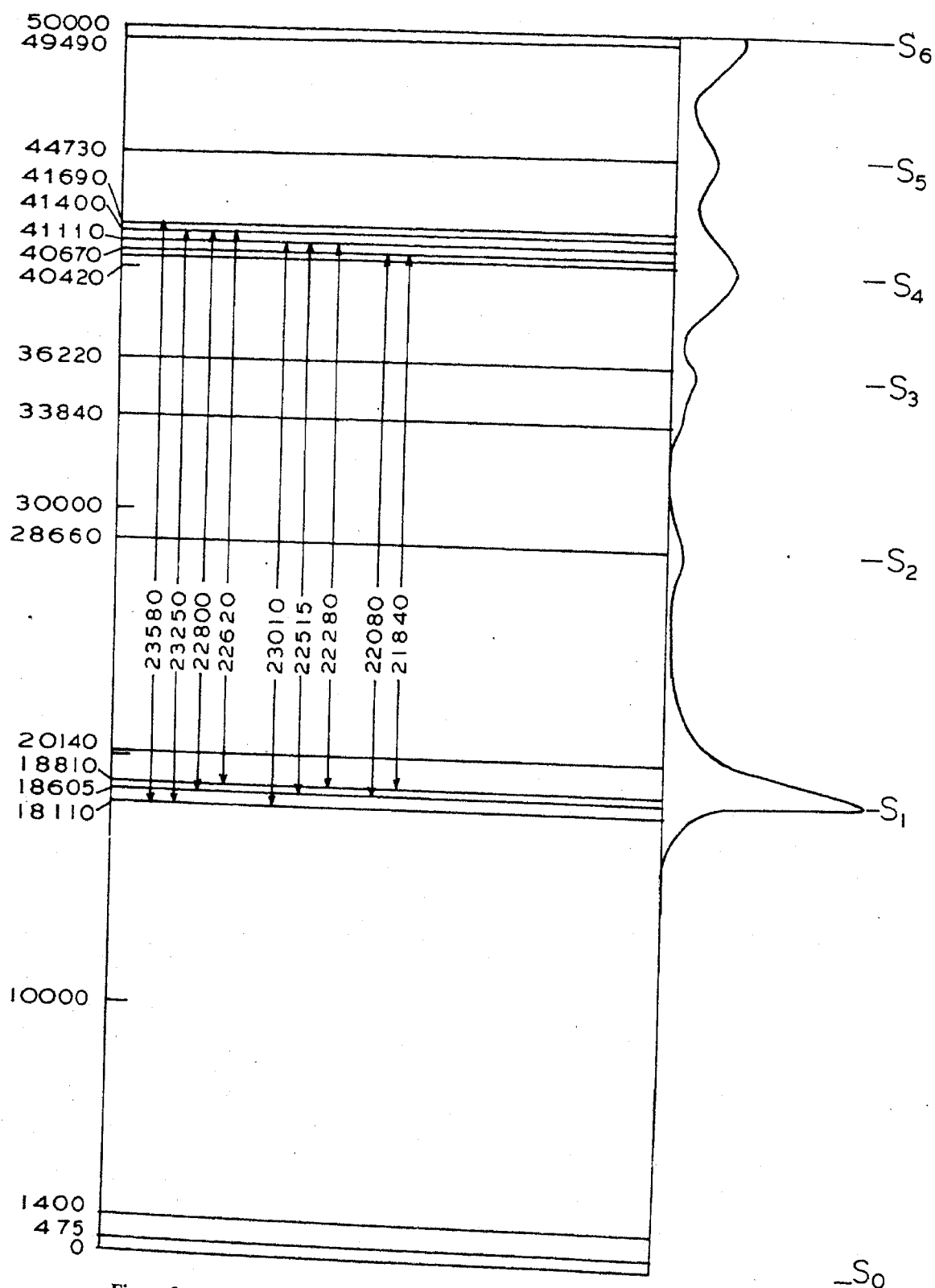


Figure 3. Energy level diagram of Rhodamine 6G.

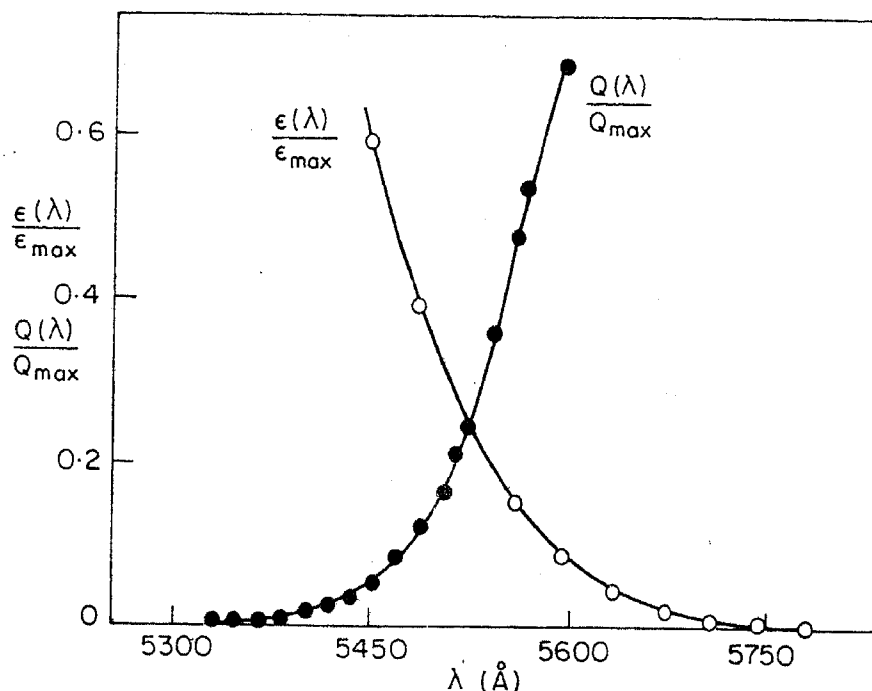


Figure 4. Absorption spectrum, $\epsilon(\lambda)/\epsilon_{\max}$ and fluorescence spectrum $Q(\lambda)/Q_{\max}$ of Rhodamine 6G.

and
$$I_2 = I_0 \exp(-(\alpha + \sigma_g(N - n) + \sigma_e n)L),$$

where L is the absorption path length, α is the linear absorption coefficient of the pure solvent, σ_g and σ_e are respectively the cross-sections for absorption out of the ground and excited singlet states S_0 and S_1 of the solute molecules at the probe wavelength and N and n are respectively the total number of solute molecules per unit volume and the number of those lifted to the S_1 state by the pump beams which are encountered by the probe beam. In the expression for I_2 the effect of stimulated emission on n at the wavelength of the probe has been neglected.*

The ground state absorption parameter is given by

$$N(\sigma_g)_\lambda L = \ln(I/I_0)_\lambda - \ln(I_1/I_0)_\lambda = \ln(I/I_1)_\lambda,$$

and the absorption cross-section relative to its maximum value,

$$(\sigma_g)_\lambda / (\sigma_g)_{\max} = \ln(I/I_1)_\lambda / \ln(I/I_1)_{\max}.$$

Similarly the relative differential absorption cross-section between the ground and the first excited singlet states S_0 and S_1 is given by

$$n(\sigma_e - \sigma_g)_\lambda L = \ln(I_1/I_0)_\lambda - \ln(I_2/I_0)_\lambda = \ln(I_1/I_2)_\lambda,$$

or

$$(\sigma_e - \sigma_g)_\lambda / (\sigma_e - \sigma_g)_{\max} = \ln(I_1/I_2)_\lambda / \ln(I_1/I_2)_{\max}.$$

* This assumption is valid in the region covered by the present study as there is no evidence of stimulated emission in this region.

Table 1. Excited singlet state absorption in Rhodamine 6G (6.7×10^{-4} M/l in ethanol) in the region, 4180–4640 Å.

Probe beam wavelength λ in Å	Pure solvent I/I_0	Solution		4	5	6	7	8	9	10
		without pump I_1/I_0	with pump I_2/I_0							
4180	5.60	2.80	2.50	0.693	0.552	0.175	0.113	0.090	0.481	
4200	8.30	4.30	3.80	0.658	0.524	0.166	0.124	0.099	0.529	
4220	10.00	5.40	4.70	0.616	0.491	0.155	0.139	0.111	0.594	
4230	10.44	5.80	5.00	0.588	0.468	0.148	0.149	0.119	0.636	
4240	10.80	6.00	5.15	0.588	0.468	0.148	0.153	0.122	0.652	
4250	10.84	6.13	5.27	0.570	0.454	0.144	0.151	0.121	0.652	
4255	11.06	6.12	5.26	0.592	0.471	0.149	0.151	0.121	0.647	
4260	11.04	6.20	5.37	0.577	0.459	0.145	0.144	0.115	0.615	
4265	10.98	6.17	5.27	0.576	0.458	0.145	0.158	0.126	0.674	
4270	10.90	6.20	5.28	0.564	0.449	0.142	0.161	0.129	0.690	
4280*	12.80	8.22	7.15	0.443	0.452	0.143	0.139	0.140	0.749	
4290*	13.02	8.10	7.00	0.475	0.467	0.148	0.146	0.146	0.781	
4300	13.30	8.10	6.97	0.496	0.496	0.157	0.150	0.148	0.791	
4305	13.50	8.11	6.98	0.510	0.510	0.161	0.150	0.150	0.802	
4310	13.68	8.13	6.96	0.520	0.520	0.165	0.155	0.155	0.829	
4315	13.80	8.14	6.93	0.528	0.528	0.167	0.161	0.161	0.861	
4320	13.80	8.16	6.90	0.525	0.525	0.166	0.168	0.168	0.898	
4330	14.00	8.06	6.80	0.552	0.552	0.175	0.170	0.170	0.909	
4340	14.00	7.96	6.65	0.565	0.565	0.179	0.180	0.180	0.963	
4350	14.00	7.79	6.50	0.586	0.586	0.185	0.181	0.181	0.968	

4360	14.00	7.52	6.28	0.621	0.621	0.196	0.180	0.180	0.180	0.963
4370	13.88	7.28	6.07	0.645	0.645	0.204	0.182	0.182	0.182	0.973
4380	13.80	7.04	5.84	0.673	0.673	0.213	0.187	0.187	0.187	1.000
4390	13.68	6.76	5.62	0.705	0.705	0.223	0.185	0.185	0.185	0.989
4440	13.60	6.50	5.46	0.738	0.738	0.233	0.174	0.174	0.174	0.930
4410	13.74	6.25	5.24	0.788	0.788	0.249	0.176	0.176	0.176	0.941
4420	13.60	6.00	5.02	0.818	0.818	0.259	0.178	0.178	0.178	0.952
4430	13.74	5.71	4.83	0.878	0.878	0.278	0.168	0.168	0.168	0.898
4435	13.74	5.60	4.72	0.898	0.898	0.284	0.171	0.171	0.171	0.914
4400	13.80	5.46	4.60	0.927	0.927	0.293	0.172	0.172	0.172	0.920
4450	13.98	5.20	4.40	0.989	0.989	0.313	0.167	0.167	0.167	0.893
4460	14.20	4.95	4.20	1.054	1.054	0.333	0.164	0.164	0.164	0.877
4470	14.36	4.66	4.00	1.125	1.125	0.356	0.153	0.153	0.153	0.818
4480*	14.60	4.40	3.80	1.199	1.199	0.378	0.147	0.147	0.147	0.802
4490*	14.90	4.18	3.60	1.271	1.271	0.402	0.149	0.149	0.149	0.802
4500*	15.20	3.90	3.40	1.360	1.360	0.432	0.137	0.137	0.136	0.727
4510	26.40	6.55	6.10	1.394	1.466	0.464	0.071	0.071	0.129	0.690
4520	26.90	6.00	5.65	1.500	1.577	0.499	0.060	0.060	0.109	0.583
4530	27.52	5.50	5.18	1.610	1.693	0.536	0.060	0.060	0.109	0.583
4540	27.85	5.00	4.75	1.717	1.805	0.571	0.051	0.051	0.093	0.497
4550	28.16	4.55	4.35	1.823	1.917	0.606	0.045	0.045	0.082	0.439
4560	28.65	4.04	3.88	1.959	2.060	0.652	0.041	0.041	0.075	0.401
4570	28.80	3.61	3.50	2.077	2.184	0.691	0.031	0.031	0.057	0.305
4580	28.95	3.23	3.13	2.193	2.306	0.730	0.032	0.032	0.058	0.310
4590	29.12	2.83	2.76	2.331	2.451	0.775	0.026	0.026	0.047	0.251
4600	29.30	2.50	2.45	2.461	2.587	0.818	0.020	0.020	0.036	0.193
4610	29.30	2.23	2.19	2.576	2.708	0.857	0.019	0.019	0.035	0.187
4620	29.30	1.92	1.90	2.725	2.865	0.906	0.011	0.011	0.020	0.107
4630	29.30	1.68	1.67	2.859	3.006	0.951	0.005	0.005	0.009	0.048
4640	29.30	1.45	1.45	3.006	3.161	1.000	0.000	0.000	0.000	0.000

* These are points in the overlap portions of two adjacent tuning ranges of the laser dyes and the corresponding absorption parameters given in columns 6 and 9 represent the average values of these quantities obtained after matching.

The normalized transmitted probe beam intensities I/I_0 , I_1/I_0 and I_2/I_0 , the absorption parameters $N(\sigma_g)_\lambda L$ and $n(\sigma_e - \sigma_g)_\lambda L$ and the relative absorption cross-section $(\sigma_g)_\lambda/(\sigma_g)_{\max}$ and the relative differential absorption cross-section $(\sigma_e - \sigma_g)_\lambda/(\sigma_e - \sigma_g)_{\max}$ are given in table 1 for Rhodamine 6G at a concentration of 6.7×10^{-4} M/l in ethanol. As the calculated values of the absorption parameters in the overlapping portions of adjacent laser dye tuning ranges are found to vary the final values of these quantities over the complete region of study have been obtained by multiplying the calculated values in different tuning ranges by appropriate matching factors. The values of $(\sigma_g)_\lambda/(\sigma_g)_{\max}$ and $(\sigma_e - \sigma_g)_\lambda/(\sigma_e - \sigma_g)_{\max}$ are plotted against the probe wavelength in figure 5. It can be seen from the figure that the relative absorption cross-section of the ground state varies smoothly with wavelength whereas the relative differential absorption cross-section varies unevenly with wavelength showing a broad maximum with a number of submaxima and shoulders. It is therefore reasonable to assume that this uneven variation arises solely as a result of the variation of the excited singlet state absorption cross-section σ_e with the probe wavelength. Accordingly, in what follows, the six submaxima at 23580, 23250, 23010, 22800, 22620 and 22515 cm^{-1} and three possible shoulders at 22280, 22080 and 21840 cm^{-1} given in table 2 are treated as excited singlet state absorption features.

Excited singlet state absorption in Rhodamine 6G was studied earlier by different groups. Dolan and Goldschmidt (1976) studied the region, 3650–4750 Å and observed a maximum at 4400 Å and a submaximum around 4000 Å. Magde *et al* (1981) investigated the region, 3000–6500 Å and reported a submaximum at 5300 Å in addition to the two reported by Dolan and Goldschmidt. Sahar and Treves (1977) investigated the region, 4600–6150 Å and reported two maxima at 5300 Å and 5650 Å, which were confirmed by Falkenstein *et al* (1978). The different maxima in the excited singlet state absorption observed by these workers are included for comparison in table 2.

The six absorption submaxima and the three possible shoulders observed in the present experiments obviously represent the vibrational structure in the broad absorption band with the maximum at about 4400 Å reported earlier by other workers. It can be seen from the energy level diagram (figure 3) that all the submaxima and shoulders can be tentatively attributed to transitions from the first excited electronic state S_1 to the electronic state S_4 at 40230 cm^{-1} . The submaxima at 23250, 22800 and 22620 cm^{-1} can be attributed respectively to the transitions from the vibrational levels at 18110, 18605 and 18810 cm^{-1} of the electronic state S_1 to a common vibrational level at 41400 ± 40 cm^{-1} of the electronic state S_4 . Similarly, the submaxima at 23010 and 22515 cm^{-1} and the shoulder at 22280 cm^{-1} could be due to the transitions respectively from the same three vibrational levels of S_1 state to another common vibrational level at 41110 ± 20 cm^{-1} of the S_4 state while the two shoulders at 22080 and 21840 cm^{-1} probably represent the transitions from the vibrational levels at 18605 and 18810 cm^{-1} of S_1 respectively to yet another common vibrational level at 40670 ± 20 cm^{-1} . These transitions are given in table 2 and are shown in figure 5. Finally, assuming that the submaximum at 23580 cm^{-1} also results from a transition involving the lowest vibrational level of S_1 , one finds the upper level to be at 41690 cm^{-1} which lies within the bandwidth of the S_4 state.

The other maxima in the ESSA observed by earlier workers are outside the region investigated here. However, transitions responsible for these maxima may be identified on the basis of the energy level diagram obtained from the present work (see table 2). The maximum at 4000 Å (24993 cm^{-1}) probably represents a transition from the S_1

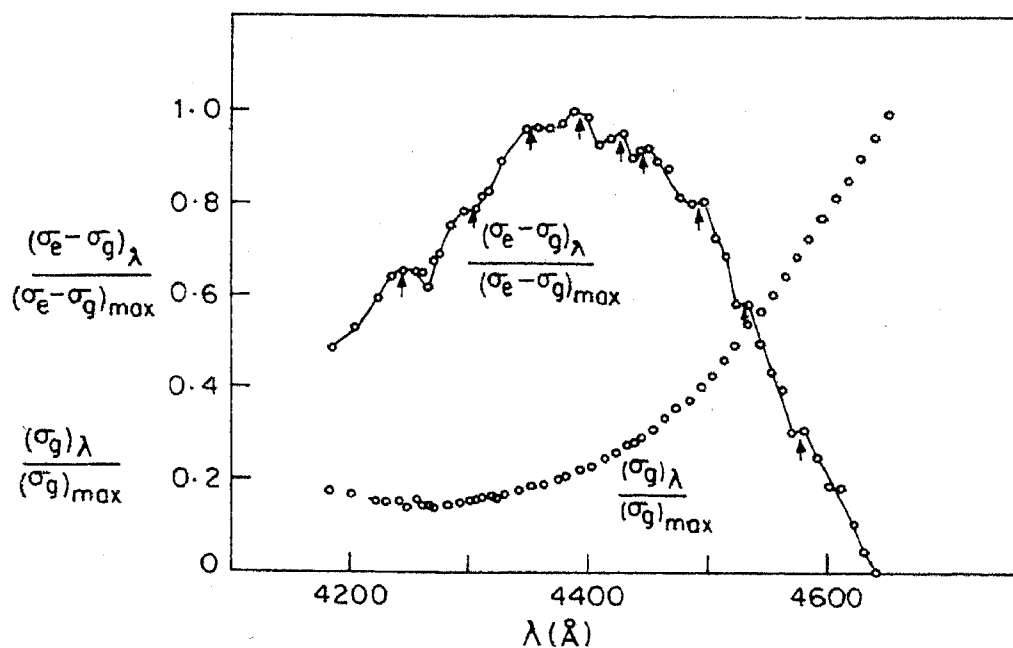


Figure 5. Excited singlet state absorption spectrum of Rhodamine 6G (6.7×10^{-4} M/l in ethanol) in the region, 4175–4640 Å.

Table 2. Transition assignments to the observed features in the ESSA spectrum of Rhodamine 6G.

ESSA Maximum submaximum or shoulder		Transition assignment					
Earlier work		Present work	Vibrational levels T_e, v (in cm^{-1})		Upper electronic state	Absorption maximum	
λ (in Å)	ν (in cm^{-1})	ν (in cm^{-1})	Lower	Upper	(S_n)	ν (in cm^{-1})	
4000*†	24990		18110	43100	S5	44730	
			23580	18110	41690	S4	40420
			23250	18110	41400 ± 40	S4	"
			23010	18110	41400 ± 20	S4	"
			22800	18605	41400 ± 40	S4	"
4400*†	22720		22620	18810	41400 ± 40	S4	"
			22515	18605	41110 ± 20	S4	"
			22280	18810	41110 ± 20	S4	"
			22080	18605	40670 ± 20	S4	"
			21840	18810	40670 ± 20	S4	"
5300†xx	18860		18110	36970	S3	36220	
5650xx	17695		18110	35805	S3	36220	

* Dolan and Goldschmidt (1976); † Magde *et al* (1981); xx Sahar and Treves (1977).

state to the electronic state S_5 at 44950 cm^{-1} . The absorption maxima at 5300 Å (18863 cm^{-1}) and 5660 Å (17663 cm^{-1}) are probably due to transitions from the electronic state S_1 to S_3 at 36220 cm^{-1} as suggested by Sahar and Treves (1977). The separation of 1200 cm^{-1} between the two absorption maxima may correspond to one of the vibrational frequencies associated with the S_3 state.

4. Discussion

As stated earlier, the excited singlet state absorption spectrum has been found to consist of a broad band with a number of submaxima and a few possible shoulders which represent the vibrational structure. It has been possible to identify tentatively all the observed features with the transitions originating in the different vibrational sublevels of the first excited singlet state S_1 and terminating in one or more vibrational levels of the upper electronic state S_4 . The spread in the energy of the vibrational levels of the S_1 state involved in these transitions is as large as 700 cm^{-1} . It appears, at first, that this is unlikely considering that all the fluorescence has been assumed to originate from the lowest vibrational level of the state S_1^* . However, in the present experiment the pump and the probe laser pulses, each of which is of 8 nsec duration, overlap each other for a period of ~ 5 nsec (as the delay introduced between the two pulses is about 3 nsec), during which they simultaneously interact with the dye molecule. Though the radiationless deactivation of the molecules in the excited vibrational levels of S_1 to its lowest vibrational level is expected to be so fast as to render the steady-state populations of these levels negligibly small, continuous production of molecules in these levels by the pump laser pulse during its entire width can maintain detectable non-equilibrium populations in them. It should therefore be possible for absorptive transitions to occur from these excited vibrational levels** in addition to those occurring from the lowest vibrational level of the S_1 state during the period of overlap of the two pulses.

But the expectation that the steady-state population of the higher vibrational levels of the S_1 state is negligible is valid only when the temperature is so low that these vibrational levels are not already thermally populated by the Boltzmann distribution of the molecules in that state. However, at the temperature at which the present experiments were conducted the S_1 state has been found to be populated up to a height of 645 cm^{-1} as demonstrated by the short-wavelength edge of the fluorescence spectrum. Since the first excited vibrational level of the S_1 state lies within the energy bandwidth of that state it is possible for that level to have a "non-negligible" steady-state population. Therefore, the submaxima or shoulders in ESSA due to transitions from the first excited vibrational level of S_1 should be somewhat stronger than the other submaxima or shoulders but weaker than those corresponding to the transitions from the lowest vibrational level. Contrary to this expectation, however, in the present studies it has been observed that the submaxima and shoulders due to transitions from the first vibrational level are almost of equal strength as those due to transitions from the lowest and the second vibrational levels of S_1 . However, since the Franck-Condon factors depend on the relative positions of the classical turning points of motion in the initial and final levels of the different transitions, it is quite possible for the transitions from the higher excited vibrational levels of S_1 to have appreciably larger values for the FCF's and hence for the corresponding submaxima and shoulders to have almost the same strength as the others.

* As shown in the following paragraph this assumption is not entirely valid.

** It may be recalled that in self-absorption, a process that affects the optimum wavelength at which the dye laser operates, thermal populations of the different vibrational levels of the ground state undergo similar transitions to the first excited state S_1 (Peterson 1979).

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