

Dye Stability Under Excimer-Laser Pumping

II. Visible and UV Dyes

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Abstract. The stability of laser dyes under the excitation of a XeCl-laser (308 nm) has been investigated. The measurements were performed in an oscillator amplifier device where the amplifier was fully saturated. This allows the comparison with the theoretical model showing that the main reason for dye degradation is the absorption of photo-products. Results for the most important dyes are presented. Dye stabilities range from 46 (fluorescein 27) to 3.4×10^4 (QUI) absorption processes per molecule before the dye solution has degraded to 1/2 of its initial energy output.

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Dye lasers pumped by excimer lasers, in particular by XeCl lasers, are ever gaining in importance. Excimer lasers offer high pulse power at high repetition rates as well as the advantage that only one pump laser is necessary for spanning the whole dye spectrum from uv to ir.

For high-average-power dye lasers, the dye stability is no less important than are efficiency and tuning range. Especially for applications demanding large amounts of photons (such as isotope separation or in experiments with low signal-to-noise ratios) the dye stability can be the determining factor whether the total process is possible or not. Because of the difference in either pump wavelength or pump power, it is hardly possible to evaluate the dye stability from data found with other types of pumping such as flashlamps, ruby, Nd:YAG or N₂ lasers.

In [1] we discussed the method of dye lifetime measurement and presented the results for some ir dyes. In this paper we shall continue the discussion by presenting measurements for the most important dyes in the visible and uv spectral ranges.

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1. Experimental Set-up

A laser-grade dye ("Lambdachrome"®) was tested in an oscillator/amplifier device (FL 2002 from Lambda Physik), pumped by an XeCl laser with energies of up to 500 mJ. Details of the experiment were described in [1]. Briefly, the last amplifier (a 2 cm wide cuvette) was the subject of investigation. For a correct interpretation of the results, it is essential that the incoming dye-laser pulse always saturates the amplifier. Therefore, all experiments were done in the center of the tuning curve of each dye where maximum amplification is achieved. The saturation condition of each dye was tested by monitoring the output energy versus input dye-laser energy. The total dye-laser energy was monitored as a function of the numbers of shots and thus as a function of the total pumping energy. Normally, the test ended when the initial energy dropped to one-half of its initial value. The experiment was performed under the following conditions:

- pulse repetition rate: 10 pps,
- pump pulse energy: 200 mJ,
- dye solution in closed circulation system at room temperature,
- volume of dye solution: 120 cm³,
- speed of circulation: 20 cm³/s, and

Table 1. Stability parameters of the various dyes

1 Dye	2 λ max [nm]	3 Solvent	4 Conc. ^a [g/l] <i>c</i>	5 pump fluence [J/cm ²]	6 Stability		8 Type of decrease	9 Dye solution deterioration			12 E/E_0 (theo.)	13 E/E_0 (exper.)	14 M_w
					Phot/mol. [p _s]	Wh [w]		$a = \frac{K_{308}}{K_{308}^{(0)}}$	$b = \frac{n_d}{n_d^{(0)}}$	K_{abs} [cm ⁻¹]			
PTP	343	di	0.4	0.56	2.4 10 ³	451	lin.-exp.	0.97	≈0.97	0.1	0.88	0.76	230
PBD	360	di	0.2	0.58	2.0 10 ³	145	linear	0.65	<0.65	0.2	0.82	0.5	298
BMQ	362	di	0.3	0.61	9.4 10 ³	912	lin.-exp.	0.9	≈0.9	0.2	0.82	0.74	334
But.-PBD	363	di	0.3	0.55	9.0 10 ³	824	linear	0.72	≈0.72	0.2	0.82	0.86	354
DMQ	364	di	0.17	0.49	2.2 10 ⁴	1209	compl.	1.1	–	–	–	0.65	334
TMI	376	di	0.21	0.67	1.3 10 ⁴	673	–	0.94	≈0.94	0.1	0.88	0.85	438
BBD	378	di	0.15	0.67	7.0 10 ³	303	linear	0.81	0.77	0.1	0.88	0.7	374
QUI	387	di	0.25	0.56	3.4 10 ⁴	1457	–	1	–	–	–	0.94	630
PBBO	396	di	0.4	0.53	2.8 10 ³	348	exponent	1	≈0.9	0.1	0.8	0.64	347
α-NPO	400	di	0.48	0.67	310	59	exponent	0.9	≈0.87	–	0.98	0.5	271
DPS	406	di	0.25	0.53	1.7 10 ³	138	<exponent	0.87	0.81	–	0.93	0.55	332
Bis-MSB	423	di	0.36	0.51	5.2 10 ³	652	–	0.95	0.85	–	0.89	0.75	310
Stilben 3	424	me	0.6	0.42	118	14	exponent	1.04	0.78	–	0.75	0.5	563
Coumarin 120	441	me	0.62	0.61	60	23	linear	1.06	0.96	0.22	0.72	0.5	175
Coumarin 2	448	me	0.85	0.61	73	31	exponent	1.27	0.85	0.2	0.55	0.5	217
Coumarin 47	458	me	1.5	0.64	64	45	exponent	1.08	0.9	0.25	0.58	0.5	231
Coumarin 102	475	me	2.4	0.66	240	244	–	–	–	–	–	0.5	255
Coumarin 307	500	me	2.2	0.61	105	92	lin.-exp.	1.46	0.82	0.15	0.52	0.5	271
Coumarin 334	520	me	1.5	0.53	400	229	linear	1	0.8	0.4	0.6	0.5	283
Coumarin 153	540	me	2	0.62	230	161	linear	1.08	0.63	0.2	0.48	0.5	309
Fluorescein 27	553	me	1.4	0.65	46	17	exponent	0.98	0.58	0.2	0.49	0.5	401
Rhodamin 6G	581	me	1.4	0.5	10 ³	316	linear	0.82	0.8	0.6	0.58	0.5	479
Rhodamin B	600	me	0.8	0.65	1.1 10 ³	144	linear	0.8	0.68	1	0.46	0.5	479
Sulforhod. B	605	me	0.9	0.58	765	198	linear	1.1	0.9	0.7	0.48	0.5	559
Sulforhod. 101	652	me	0.78	0.53	2.5 10 ³	133	–	0.87	0.55	0.15	0.57	0.68	606
DCM	658	DMSO	0.43	0.48	250	348	exponent	1.1	0.82	0.2	0.59	0.5	303
Furan 6	700	me	0.6	0.53	600	38	–	–	–	–	–	–	421
Nilblau-sulf.	703	me	0.5	0.6	512	92	linear	1	0.9	0.6	0.52	0.5	354
Oxazine 170	708	me	0.78	0.62	2.5 10 ³	488	57% incr.	–	–	–	–	–	432
Pyridin 1	710	DMSO	0.72	0.21	570	117	lin.-exp.	1.13	0.82	0.1	0.6	0.65	378
Rhodamin 700	722	me	0.66	0.64	600	80	lin.-exp.	0.7	0.42	–	0.59	0.5	538
Oxazine 1	728	me	0.7	0.61	120	25	linear	0.96	0.96	0.5	0.63	0.5	360
Oxazine 750	775	DMSO	0.67	0.43	10 ³	154	14% incr.	1.65	0.17	0.1	0.1	0.5	470
Styryl 9	840	DMSO	1	0.22	356	73	linear	1	0.64	–	0.64	0.5	528

^a Oscillator concentration. Amplifier concentration equals to 1/3 of this value

f) the dye solution was filtered with a “Balston Filter”, grade B.

Before and after the exposure to the pump laser, the dye solution was spectroscopically investigated. The absorption in the uv and ir spectral ranges, especially the change in the absorption at the pump wavelength and at the laser wavelength, was compared.

2. Results

Thirty-four different dyes were investigated, the results of which are given in Table 1. The names of the dyes are quoted according to Lambda Physik's notation (column 1); they are listed according to their wavelength, starting with the uv dyes. The wavelength of the

maximum laser energy (column 2) depends on the type of solvent (column 3) and on the concentration. Column 4 gives the concentration used in the oscillator and preamplifier, while the concentration in the final amplifier is normally three times less than this value. The wavelength of the maximum laser energy denoted in column 2 is found under these conditions. Column 5 describes the pump energy density of the final amplifier. The small variations of this value reflect changes of the pump-laser energy during the course of the experiments. Normally, about 0.2 Joule were focused to a strip of 2 × 0.2 cm² of the dye cuvette entrance. As shown in [1], the dye stability of polymethene dyes is not critically dependent on this value; the same was found with the dyes given in Table 1.

Lastly, the dye stability is described in two different ways. Column 6 presents a more or less physical interpretation by denoting the number of pump photons which can be absorbed per dye molecule before the output energy of the solution has degraded to 50% of its initial value. Because the output energy depends also on absorption processes by the photofragments, it does not always describe the stability of the dye molecule itself. This matter will be discussed in more detail below. Nevertheless, the term dye stability is used here, in the sense of the stability of the dye solution. Column 7 gives, for practical reasons, the total energy which can be pumped into the dye laser (FL 2002) with one liter of dye solution in the amplifier before the energy has dropped to 50% of its initial value. This is the Watt-hour value often quoted by dye suppliers, which can easily be calculated from the concentration c , the dye stability in photons/molecule p_s and the molecular weight M_w (column 4) by

$$w = 1.08 \cdot 10^2 \cdot \frac{c \cdot p_s}{M_w} [\text{Wh}]. \quad (1)$$

(The numerical value $1.08 \cdot 10^2$ comprises energy conversion factors and Avogadro's number.)

Column 8 describes, in a more qualitative way, the type of decrease found for the dyes. Some of the dyes show a strictly linear decrease in laser energy (or efficiency) with respect to the pump energy, while others behave exponential. No general rule can be established; and where the decrease is neither linear nor purely exponential, the classification "linear-exponential" is used.

The evaluation of the absorption spectra is given in the next three columns 9, 10, and 11. The quantity $a = k_{308}/k_{308}^{(0)}$ describes the change of absorption coefficient at the pump wavelength during the experiment ($a=1$ means that no change has occurred). The value $b = n_{\text{dye}}/n_{\text{dye}}^{(0)}$ is a measure of the change of the dye density with respect to the initial value. This so-called bleaching factor b was calculated from the change in the absorption band S_0-S_1 , which is normally not influenced by the photofragment absorption bands. Column 12 will be discussed in the next section; it describes the decrease of dye-laser energy under the condition in which the absorption spectra (data in columns 9–11) have been taken.

3. Discussion

The dye stability (Table 1, column 6) of different dyes varies over a wide range, from 46 (Fluorescein 27) to 3.4×10^4 (QUI) possible photon absorption processes per molecule. The corresponding pump energy values for one liter amplifier solution are 17 Wh and

~ 1450 Wh, respectively. The latter figure means that a 1 l dye solution can be operated for 725 h (or ≈ 120 days at a 6-h per diem rate) under the conditions of our experiment (0.2 Joule at 10 pps = 2 W average pump power). Normally, the pump-energy values quoted by the dye-laser manufacturer refer not to the input energy to the dye cell but to the total dye laser. Because only a fraction of the total input energy is used for pumping the last (saturated) amplifier cell, these more practical values can differ by a factor of nearly 2 from the more physical values given above. Figure 1 shows the dye stability for the dyes listed according to wavelength. UV dyes are the most stable, as they are pumped into the S_1 -state.

Surprisingly, the stability does not decrease drastically when the dyes are pumped in higher S -states. Some red dyes, such as Rh 6G, Rh B, Sulforhodamin 101, Furan 6, Oxazine 170 and Oxazine 750, are very stable with more than 500–1000 photons per molecule, i.e. more than 100 Wh. In contrast, Stilben and some Coumarins offer only a poor stability. This different behavior is probably due to the chemical properties of the molecules and cannot be explained by general arguments.

According to the model developed in [1], the decrease in dye-laser energy is strongly related to the absorbance of the molecules formed during the pump process. If one takes full saturation into account, the dye-laser energy following the last amplifier can be expressed by

$$E_{\text{las}} = \gamma \cdot N_p \frac{K_d}{K_d + K_{\text{ph}}} \frac{1 - \exp(-K_{\text{abs}} \cdot x_0)}{K_{\text{abs}} \cdot x_0}, \quad (2)$$

where E_{las} is the number of dye-laser photons/pulse, γ the dye efficiency, N_p the number of pump photons/pulse, K_d the absorption coefficient of dye molecules at the pump wavelength, K_{ph} the absorption coefficient of photoproduct molecules at the pump wavelength, K_{abs} the absorption coefficient of photoproduct molecules at the laser wavelength, and x_0 the length of the amplifier cuvette.

Using the parameter $a = K_{308}/K_{308}^{(0)}$ and $b = n_{\text{dye}}/n_{\text{dye}}^{(0)}$ one gets the expression for the energy decrease:

$$\frac{E}{E_0} = \frac{b}{a} \frac{1 - \exp(-K_{\text{abs}} \cdot x_0)}{K_{\text{abs}} \cdot x_0}. \quad (3)$$

According to this formula, one can predict the energy decrease solely by measuring the absorption spectra of the dye solution. In Table 1 the experimentally observed energy decrease (column 13) is compared with the decrease according to (3), taking into account only the change of the absorption spectra. As one can see, the model allows a correct prediction within $\pm 20\%$ for more than 80% of all dyes investigated.

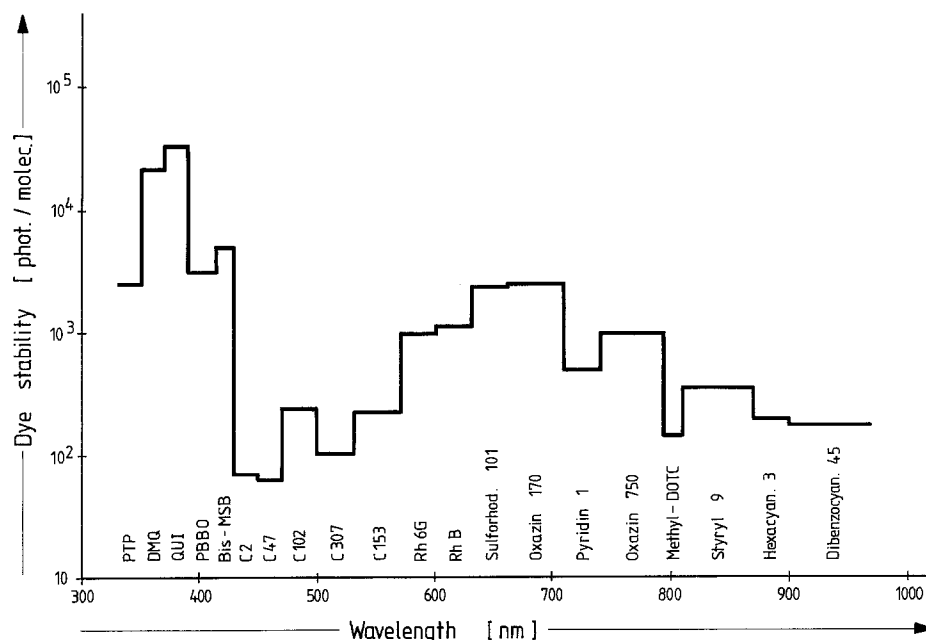


Fig. 1. Dye stability in photons per molecule which can be absorbed before the dye solution had degraded to 50% of the initial energy value

Table 2. Comparison of stability values for several dyes under XeCl-excimer pumping, compared in this work with other literature data

Dye	Solvent	Stability [Phot./mol.]	
			This work
PTP	di	$2.6 \cdot 10^3$ (2)	$2.4 \cdot 10^3$
PBD	di	$5.2 \cdot 10^3$ (2)	$2.0 \cdot 10^3$
		at $5 \div 15$ MW/cm ²	at 23 MW/cm ²
BBD	di	$8.3 \cdot 10^3$ (2)	$7.0 \cdot 10^3$
α -NPO	di	22 (2)	310
	cyclohexane	210 (2)	

By investigating the factors a and b one can determine the relative influence of the bleaching (described by b) and the photofragment absorption on the energy decrease.

For example, in the case of Sulforhodamin 101 and Rhodamin 700, the bleaching is faster than one would expect solely on the basis of the energy decrease. This is due to two facts: a) in normal dye lasers the amplifiers are driven above the saturation limit, and the incoming oscillator pulse fills a broader cross-section than that of the active volume, so that decreases in dye concentration result only in increases in the pump-beam penetration depth with a nearly constant number of dye molecules in the active volume; b) the absorption of the photofragments (column 11) at the laser wavelength is nearly negligible.

For most dyes the decrease in laser energy is mostly due to the absorption of photoproducts at the laser wavelength and/or of the pump wavelength. This

means that the real lifetime of the dye molecules can be much longer than observed in the experiments. The photofragments only spoil the solution by their absorption. A prominent class of these dyes is the Coumarins, in which the solution degrades to 50%, whereas the dye molecules are destroyed by merely 10–20%. Here, the degradation is mainly due to the laser radiation absorption. The same is true for most of the Rhodamines; they exhibit a strong absorption by the photoproducts at the laser wavelength. Here, in addition, one observes a decrease, too, in the pump radiation absorption.

Table 2 gives a comparison of the data measured by Cassard et al. [2] and our data. Most values are in quite good agreement. The difference for PBD can be explained in part by the higher pump-power density used in our experiments. For α -NPO the discrepancy is quite striking. The molecule itself seems to be stable, and we suppose that impurities have led to the low stability in the dioxane solution. Our data are in reasonable agreement with their data on cyclohexane.

While the energy decrease of most dyes can be explained through the influence of the photofragments, there are some dyes which do not fit into this scheme. α -NPO and DPS, for example, show an exponential decrease which is not a result of the absorption of photoproducts. Here, the model fails, i.e. the assumptions made are not applicable to these dyes. The photofragments probably have absorption spectra similar to those of the dye. Consequently, determination

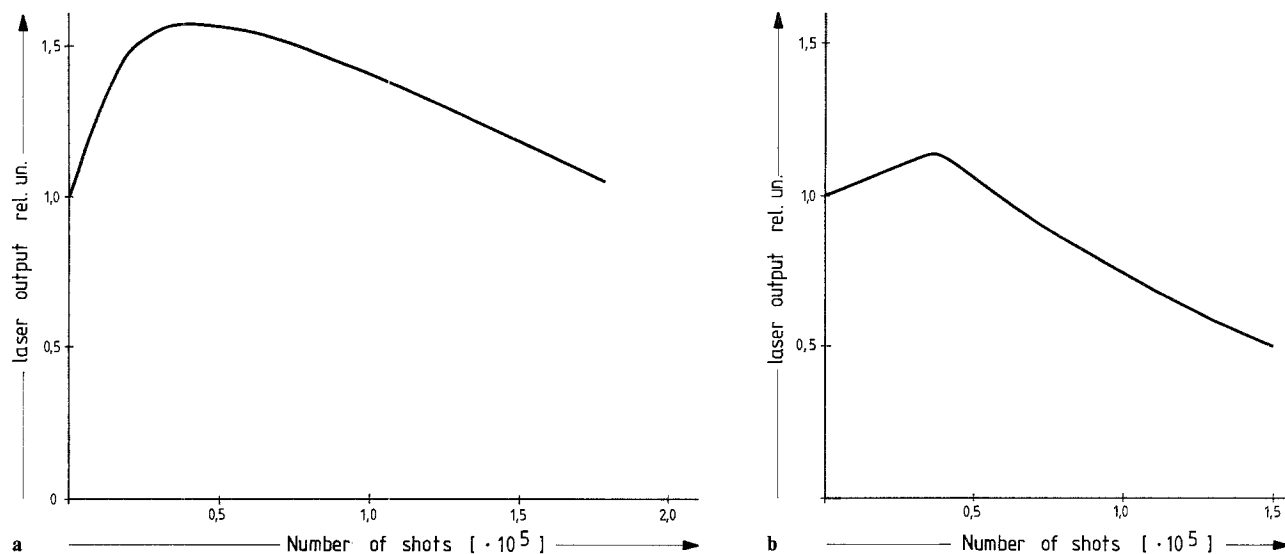


Fig. 2a and b. Dependence of the laser energy of (a) Oxazine 170 ($\lambda = 708$ nm) and (b) Oxazine 750 ($\lambda = 775$ nm) on the number of laser shots at pump intensities of 25 MW/cm² (a) and 17 MW/cm² (b)

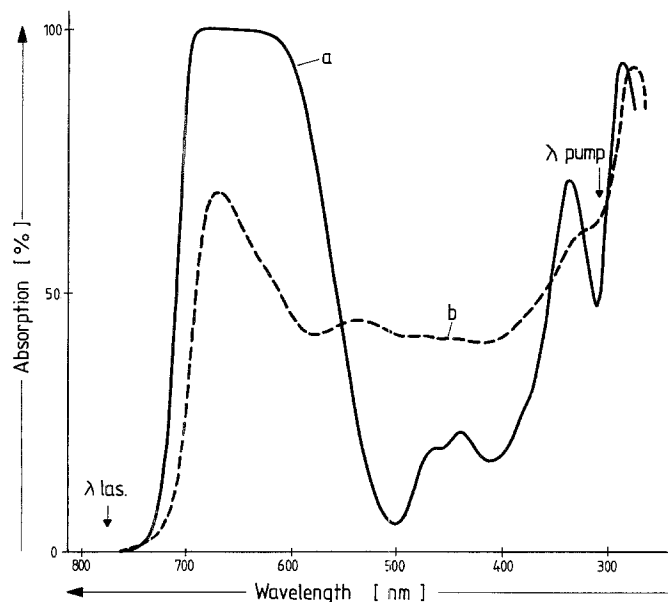


Fig. 3. Change of the absorption spectra in Oxazine 750. Curve *a* denotes the spectrum before the experiment, Curve *b* after the dye solution has degraded to 50% of its initial value

of dye bleaching from absorption measurements is incorrect. Some of the oxazines behave very strangely: Instead of an energy decrease, one observes an energy increase.

Figure 2 shows the energy dependence for Oxazine 170 and Oxazine 750 on the number of laser pulses. The energy increase reaches a maximum after some 4×10^4 laser pulses and decreases nearly exponentially later on. This abnormal behavior is accompanied by a strong change in the absorption spectra, indicated in Fig. 3 for Oxazine 750. If one supposes the dye concentration to be proportional to the absorption of the

S_0-S_1 band, one finds that more than 80% of the original dye molecules have been destroyed. On the other hand, a new compound, the photofragments, show strong absorption at $\lambda = 400-500$ nm. Similar dependences are found for Oxazine 170 and Oxazine 1.

A possible explanation for this strange performance is the formation of a new dye, which means that the photofragments or the reaction products of the photofragments form new dyes. These new dyes can also be pumped by XeCl-laser radiation and emit in the same spectral range as the original dye. Evidence for this is

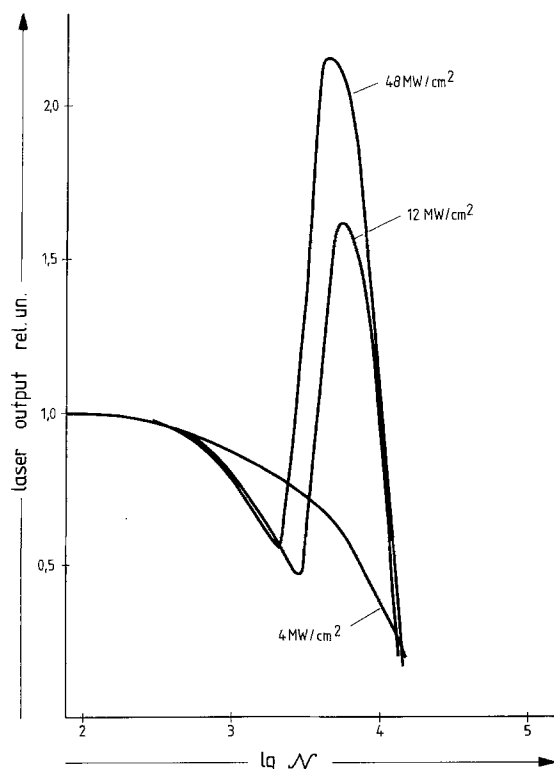


Fig. 4. Output energy of Oxazine 1 in a simple oscillator arrangement with respect to the number of laser pulses. The various pump powers are indicated on the three curves

to be found in oscillator measurements. Oxazine 1 was placed between two broad-band mirrors and the output energy monitored with respect to the shot number. After several thousand shots, the energy increases drastically (Fig. 4), reaches a maximum which can be twice the amount of the initial energy and finally drops very strongly. This peak in laser energy depends on the pump power density as indicated by the curves in Fig. 4. The higher the pump power density, the more energy which can be found in the second peak. At lower peak power $P=4 \text{ MW/cm}^2$, the peak totally disappears and the dye behaves quite normally. One explanation for this could be a formation process for the new dye which relies on a multi-photon transition.

A more thorough study of these processes would go beyond the scope of this article. The above demonstrates, however, how complex the processes occurring during the course of the excitation and lasing of dye molecules can be.

4. Summary

We have investigated the stability of the most important dyes under the influence of XeCl-laser pumping. The reasons for the decrease in laser performance are, in general, very complex. For most dyes studied in this context it was possible to attribute the decrease to the absorption of the photofragments or photoproducts, which are accumulated in small amount during each excitation pulse. The absorption of these photoproducts can be either at the pump wavelength or at the laser wavelength. Particularly because the latter cannot be saturated, it hinders the laser output very effectively. For most dyes, this is the reason for the energy decrease. The dye molecule stability itself is in most cases better than indicated by the energy decreases.

UV dyes show the most stable performance, a fact which is not surprising in the light of the excitation being to the S_1 state. The reason for the poor stability of the Coumarin dye solutions lies not only in the dye molecule itself but also in the absorption of the photofragments at both the pump and dye-laser wavelengths. In spite of being pumped into higher S -states (S_2, S_3), red and infrared dyes normally exhibit a high stability against dissociation. Degradation is mostly due to the strong absorption of the photoproducts at the laser wavelength. Some dyes (Oxazine 1, 170, 750) show an unusual behavior, which can be explained by the formation of a new dye during the photofragmentation process.

References

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