LASER INVESTIGATION OF SOME OXAZOLE AND OXADIAZOLE DERIVATIVES

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Summary

Fast spectroscopy experiments have been performed on oxazole and oxadiazole compounds. Transient absorption from the first excited singlet state, extinction coefficients of the triplet–triplet spectrum and intersystem crossing rate constants are reported. Direct evidence of the singlet state quenching by oxygen has been obtained. These results make it possible to discuss the stimulated emission of these molecules.

Introduction

In recent years, using lasers as an actinic source, the time resolution of the molecular spectroscopy of excited states has been improved by many orders of magnitude [1 - 4]. Several kinds of experiments have been introduced which illustrate the possibilities of such techniques: picosecond and nanosecond absorption, flash photolysis, laser-induced fluorescence, temperature effects, quantum yield determination etc.

The discovery of laser emission in organic compounds [5] and the use of dyes as intra-cavity saturable absorbers in passively mode-locked lasers [6] have led to many studies in an attempt to gain a better understanding of the molecular processes in excited states and to improve the efficiency of dye lasers or the ability to generate picosecond pulses.

With this aim different photophysical aspects of excited states have been investigated including triplet absorption [7, 8], photoisomerization processes [9 - 11] and fluorescence quenching [12]. Generally, the partial results obtained from these investigations have been used successfully to explain the characteristic properties of dyes under flashlamp or laser excitation.

A more attractive way to approach this kind of study would be to investigate the dynamics of the excited states of the laser molecules in order to obtain a thorough knowledge of their photophysical behaviour. It is evident that the results of such studies may be very useful when the laser properties of these molecules are of interest.

In this paper we report detailed measurements which have been obtained from picosecond and nanosecond spectroscopy of oxazole and oxadiazole derivatives. These experiments were made in the general context of our interest in laser action in dyes [11, 13 - 15] and especially in the primary photophysical processes involved.

The present work allows the typical characteristics of the laser action of these molecules to be described in relation to their transient absorption.

Experimental

Oxazole and oxadiazole derivatives are generally known as organic scintillators because of their use in the counting of ionizing particles in nuclear physics.

Several authors [16, 17] have found that scintillators are difficult to pump by flashlamp systems and therefore have had to develop perfectly coaxial devices with fast risetime to obtain their stimulated emission. These observations suggest that substantial transient absorptions arise within the lasing wavelength range of these molecules. In particular, the strong dependence of the laser gain on the pumping risetime indicates the presence of a build-up of excited molecules in a transient state when slow pumping is used; in these conditions the stimulated emission may be obtained before the transient state is significantly populated. Since the fluorescence quantum yields of the compounds are known to be high, a transient state (*e.g.* a triplet) would not be the only state responsible for the quenching of the laser emission. Moreover, in a fast excitation device (*i.e.* a N_2 laser) where the triplet population cannot be predominant, high lasing thresholds are obtained [18] compared with other laser molecules. The only reasonable explanation is thereby to assume substantial quenching effects of the first excited singlet state owing to absorptions towards higher excited singlet states.

Materials

Scintillator grade chemicals were purchased from Koch-Light Co. and used without further purification. All solvents were commercial products of the highest grade available.

Some spectroscopic properties and laser wavelengths of the molecules studied are reported in Table 1.

Apparatus

Several kinds of fast spectroscopy experiments were performed to detect the transient states of these molecules. A fast photolysis apparatus allowed observations below the 10 ns timescale. However, for measurements in the fluorescence band a picosecond spectroscopy technique was required.

The laser (Fig. 1)

The laser consists of a ruby rod placed between two reflectors. The oscillator output is mode-locked by cryptocyanine (SA). A train of approxi-

TABLE 1

Spectroscopic properties (in benzene solutions) and lasing wavelengths of the scintillators studied

	λ_{max}^{abs}	λ_{max}^{fluo}	Φ^{fluo}	τ^{fluo}	Lasing wavelength		
					Flash pumping [16, 17]	N_2 pumping [18]	Mode-locked laser pumping*
BBO	350	410	0.75 t	1.2	410 b 410 d	408 - 435 d	410 b
PPO	310	365	0.8	1.4	381 d	360 - 381 t	381 b
α-NPO	340	400	0.94	2.0	400 e 401 d	394 - 430 d	400 b
PBBO	320	395	–	–	–	–	395 b
BBOT	375	430	0.74	1.1	437 b 433 d	431 - 436 d	435 b
α-NPD	328	370	0.7	2.0	–	372 - 391 b	374 b
PBD	305	360	0.8	1.2	360 e	357 - 376 t	376 b
PPD	280	355	0.9	1.5	348 d	–	–

Symbols: b benzene, d dioxan, e ethanol, t toluene, * present work. Abbreviations: BBO 2,5-dibiphenyloxazole, PPO 2,5-diphenyloxazole, α-NPO 2-α-naphthyl-5-phenyloxazole, PBBO 2-biphenyl-phenylbenzoxazole, BBOT 2,5-bis(tertbutylbenzoxazoleyl(2))thiophene, α-NPD 2-α-naphthyl-5-phenyloxadiazole, PBD 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole, PPD 2,5-diphenyloxadiazole.

mately 6 - 7 pulses each of half-duration 300 ps separated by nearly 10 ns was coupled out through the partially transmitting front mirror of the oscillator cavity. The train of pulses was then amplified by a factor of about ten and directed to an angle phase-matched potassium dihydrogen phosphate (KDP) crystal generating the first harmonic (347 nm). A dielectric mirror, which reflects the 694 nm light and simultaneously allows the 347 nm light to be transmitted, was placed after the KDP crystal. A 694 nm cut-off filter was added to remove any red light which may be transmitted by the reflector. The output energy was 50 - 100 mJ and the excitation power density may reach 50 MW cm^{-2}.

Picosecond spectroscopy device

The experimental set-up is depicted in Fig. 1; it involves an analysis beam produced by the laser emission of several fluorescent dyes (FD) chosen in order to investigate the spectral range 347 - 430 nm in an analogous way to that described in ref. 13. The blue laser beam is divided by the splitter L. One part is used to excite the sample and the other as a pumping source of the FD to produce the interrogating beam. A second beam splitter directs a small fraction of this light to the photodiode P_2.

The experimental procedure involved transmission measurements for each pulse of the train, first with the pumping train blocked before striking the sample (T_0) and then with the excitation present (T). The difference between the transmitted probe pulses in these two cases contains information on the excited state absorption. The signal recorded by the photodiode P_2
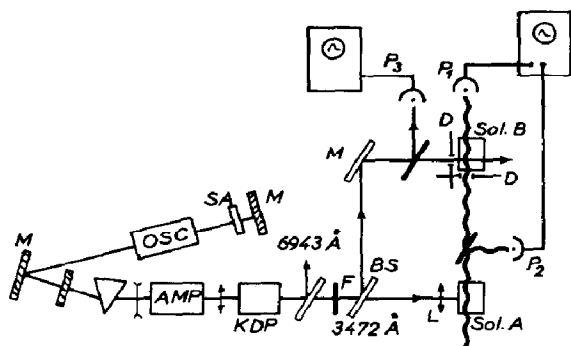
Fig. 1. Experimental set-up for picosecond spectroscopy. The symbols are defined in the text.
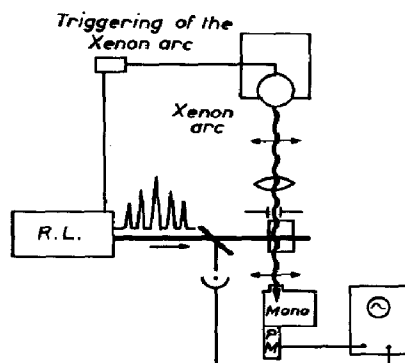
Fig. 2. Laser photolysis device.

was used as a reference in order to detect fluctuations of the analysis beam. The two signals of the photodiodes P_1 and P_2 were displayed on a Tektronix 7904 scope after being optically delayed. A third photodiode P_3 allowed the monitoring of small energy variations in the UV output of the excitation beam.

Laser photolysis apparatus

The photolysis apparatus is described in detail elsewhere [11]. The mode-locked ruby laser is used as the excitation source; the analyzing system is typically disposed in a transverse arrangement to the pumping beam (Fig. 2). The sample is contained in a fluorimetry cell. A set of diaphragms permits the selection of the homogeneous part of the excited solution.

For excited state absorption measurements, a high pressure xenon arc XBO 150 W is connected to a detection system (M25 Huet monochromator, RCA XP 1005 photomultiplier, Tektronix 7904 oscilloscope). The photo-multiplier was operated with only six stages and the risetime of the detection system was 2.3 ns when terminated at 50 Ω. To improve the signal-to-noise ratio, the current through the xenon lamp was increased for a period of 500 μs resulting in a 25 - 200 fold increase in light intensity, depending on the wavelength.

Results and discussion

Investigations of the process in the excited states

The generation of transient absorptions under the excitation of the picosecond ruby laser was investigated over the range 350 - 800 nm. The solute concentration in benzene was chosen so that an optical density of 0.5 - 1 was obtained across a 1 cm path (4×10^{-5} - 4×10^{-4} M). All the molecules studied exhibited the same behaviour. Typical oscillograms are shown in Fig. 3 as a function of the probing wavelength. Two distinct species can be identified in the wavelength range studied. The first one can be detected in the long wavelength range (530 - 800 nm depending on the molecule)
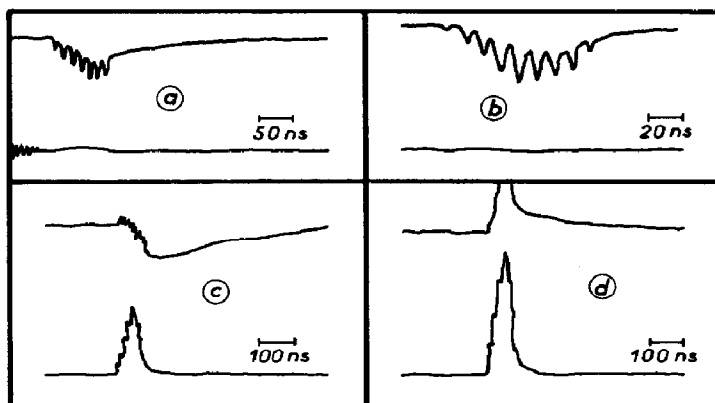
Fig. 3. Typical oscillograms of transient absorptions (a, b, c) and depletions (d) observed in BBO solution (optical density at 347 nm, 0.5; solvent, benzene).

and occurs during the excitation. The relaxation of this transient has the shape of the pumping picosecond train. The lifetime of this species (less than 3 ns)' appears to be determined by the response time of the detection system. Since the low concentrations used rule out the possibility of excimer generation, this absorption is assumed to take place between the first and any one of the higher excited singlet states. At shorter wavelengths (400 - 650 nm) a second transient species is apparent. In this region a build-up of absorption occurs over the running time of the excitation, after which the transient absorption decays by first order kinetics with a rate constant of about (2 - 5) $\times 10^6$ s^{-1}. In de-aerated solutions the lifetimes become longer than a few microseconds. It seems reasonable to assign this absorption to the triplet state.

Moreover, the triplet concentration is observed to be higher in aerated solution than in oxygen-free solution; this is related to a quenching effect of the first excited singlet state which is a function of the oxygen concentration in the solvent. As has been observed for polycyclic compounds, this effect quenches the fluorescence emission and enhances the intersystem crossing [20].

The results are summarized in Table 2 where the wavelengths of the triplet–triplet absorption maxima and the absorption wavelength ranges of the first excited singlet states are reported. Typical spectra are shown in Fig. 4 for the case of PBBO. The quenching rate constant k_T can be deduced from the triplet state lifetime τ_T. $\tau_T = (k_T [O_2])^{-1}$ with $[O_2] = 2 \times 10^{-3}$ M [19].

Depletion signals around the laser wavelength were observed in the fundamental absorption bands of the molecules α-NPO, BBO, PBBO, BBOT and α-NPD. The optical density should return to its initial value within the time required for the excited molecules to relax. For PPO, PBD and PPD such measurements were not performed because the molecules exhibit very weak extinction coefficients around 347 nm.

Measurements of the extinction coefficients ϵ_{TT} were obtained by comparison of the triplet absorption d_T and the fundamental singlet state S_0 depletion d_{01}. We can write

TABLE 2

Excited states characteristics measured by fast spectroscopy experiments

Molecule	λ_{T-T}^{max} (nm)	$\epsilon_{T-T}^{max} \times 10^{-4}$	$\lambda_{S_1-S_n}$ (nm)	τ_T (ns)	$k_T \times 10^{-9}$ $(M^{-1} s^{-1})$	TT^O (%)	TT (%)
PPO	570	–	530 - 620	200	2.5	–	–
α-NPO	550	10	650 - 800	215	2.3	0.10	0.12
BBO	560	11	600 - 800	285	1.7	0.05	0.07
PBBO	560	4.5	580 - 700	325	1.5	0.06	0.13
BBOT	520	16	620 - 770	240	2.1	0.09	0.10
α-NPD	580	6.7	600 - 700	300	1.6	0.07	0.07
PBD	510	–	550 - 720	460	1.0	–	–
PPD	550	–	640 - 710	300	1.6	–	–

The quantities TT^O and TT are the relative triplet concentrations for the de-aerated and aerated solutions, respectively, measured at time $t = 100$ ns.
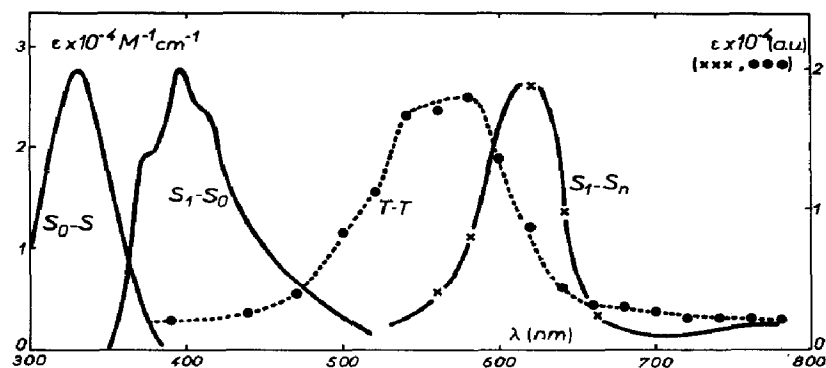
Fig. 4. T–T and S_1–S_n spectra of PBBO in benzene.

$$d_T = \epsilon_{TT} c_T l$$
and
$$d_{01} = \epsilon_{01} c_i l$$

where c_T is the concentration of the molecules in the triplet state and c_i refers to the molecules which were removed from S_0.

Assuming that the triplet extinction is weak enough to be disregarded at the wavelength where the depletion is recorded, the upper limit of ϵ_{TT} can be deduced:

$$\epsilon_{TT} = \epsilon_{01} \frac{d_T}{d_{01}}$$

Estimates of the intersystem crossing rate constant k_{ST} were obtained in the following way. Let us consider a three level system: two singlet states (S_0 and S_1) and a triplet state (T). Owing to the experimental conditions, the possibility of a significant excimer generation or of any other substantial bimolecular process is avoided in the concentration range used.

The rate equation system can be written, for each pulse number i,

$$\frac{dN_1^i}{dt} = \sigma_a N_0^i P_0^i - \frac{N_1^i}{\tau}$$

$$\frac{dN_T^i}{dt} = k_{ST} N_1^i - \frac{N_T^i}{\tau_T}$$

$$N_0^i + N_1^i + N_T^i = N$$

Here P_0^i is the pumping power density in ph cm^{-2} s^{-1} if the excitation pulse is assumed to behave as a δ function, σ_{01}, σ_{1n}, σ_{TT}, σ_e are the S_0–S_1, S_1–S_n, T_1–T_n absorption and stimulated cross sections at the analysis wavelength, respectively, σ_a is the S_0–S_1 absorption cross section at 3472 Å, τ, τ_T are the S_1 and T_1 lifetimes, k_{ST} is the intersystem crossing rate constant and N_0, N_1, N_T are the population densities (cm^{-3}) of S_0, S_1, T_1.

From the second differential equation, we obtain the triplet population generated by i pulses:

$$N_T = \sum_i \int N_T^i \, dt$$

$$= k_{ST} \tau_T^2 \sum_i \int N_1^i(t) \; \frac{\exp(-t/\tau_T) + t/\tau_T - 1}{t} \; dt$$

Hence the experimental triplet optical density d_T is assumed to be proportional to k_{ST} and ϵ_{TT} (the extinction coefficient ϵ_{TT} is related to the absorption cross section σ_{TT} by the relation $\epsilon_{TT} = 2.6 \times 10^{20} \sigma_{TT}$) and

$$d_T = k\epsilon_{TT} k_{ST}$$

The triplet lifetimes in aerated and de-aerated solutions are not the same. The proportional term k is therefore different in these two cases. In fact, the triplet optical density is measured at its maximum ($t = 100$ ns) and does not image exactly the total concentration of triplets generated by the laser pumping when τ_T is about 200 - 400 ns.

In order to compare the calculated triplet optical density with the experimental data, we calculated the triplet population using the expression

$$N_T = \sum_i N_T^i \exp(-t_i/\tau_T)$$

where N_T^i is the total triplet population generated by the pulse number i, τ_T the triplet state lifetime and t_i the time between the moment where the ith pulse strikes the sample and $t = 100$ ns. Assuming that each pulse generates the same triplet population, the following expressions may be deduced:

$$d_T^{N_2} = \alpha \epsilon_{TT} k_{ST}^0$$

$$d_T^{air} = \alpha \epsilon_{TT} k_{ST} \left\{ \sum_i \exp(-t_i/\tau_T) \right\}^{-1}$$

The quenching rate constant k_S of the first excited singlet state S_1 according to the pathway $S_1 \rightarrow T_1$ is related to k_{ST}^0 and k_{ST} by the expression [19] $k_{ST} = k_{ST}^0 + k_S[O_2]$ with $[O_2] = 2 \times 10^{-3}$ M.

TABLE 3

Intersystem crossing rate constants for some scintillators

	PPO	BBO	α-NPO	PBBO	BBOT	α-NPD	PBD
ρ	1.4	1.4	1.2	2.1	1.0	1.0	1.25
$k_{ST}^0 \times 10^{-7}$ (s^{-1})	7.5	7.5	9.5	4	20	20	10
$k_{ST} \times 10^{-7}$ (s^{-1})	13	13	15.5	10	25	25	16

It follows that

$$k_{ST}^0 = k_S[O_2] \{\rho \sum_i \exp(-t_i/\tau_T) - 1\}^{-1}$$

with $\rho = d_T^{air}/d_T^{N_2}$.

The k_{ST} estimations are reported in Table 3 assuming $k_S = 3 \times 10^{10}$ M^{-1} s^{-1} which is of the order of magnitude of singlet quenching rate constants for polycyclic compounds [20]. The yield of triplet state scintillator molecules generated during the pumping picosecond pulses can be calculated from the magnitude of the triplet generation rate constant and the observed lifetime of the first excited singlet state. As can be seen from Table 1, the lifetimes are in the range 1 - 2 ns. Thus the intersystem crossing quantum yields are typically in the range 0.2 - 0.3. These results can be used in combination with the fluorescence quantum yields (Table 1) to show that the principal ways of deactivation of the scintillator excited singlet state are a radiative process towards the fundamental singlet state and a rapid intersystem crossing.

Transient investigations were performed in concentrated solutions (10^{-3} - 10^{-2} M). Since in these experiments no absorptions (except the triplet state itself) were observed, it must be concluded that bimolecular processes are of very small importance. This is in agreement with previous fluorescence measurements made by Lami *et al.* [21].

However, in the case of de-aerated solutions the triplet state exhibits mixed order kinetics of relaxation, yielding values of 10^3 s^{-1} and 10^{10} $M^{-1}s^{-1}$ for the first and second order decay constants (these values fit satisfactorily the measurements of Dempster [22] in the case of PPO).

S_1-S_n absorption in the fluorescence band

As shown above, an absorption between the excited singlet states in a wavelength range where no light emission occurs can easily be detected by laser photolysis.

For measurements at the wavelength of the lasing emission of the molecule (near the fluorescence peak) the conventional laser photolysis system becomes inoperant and we use a picosecond spectroscopy device. The interrogating wavelength for a given molecule corresponds to its lasing wavelength. When it was difficult to obtain good reproducibility of the analysis beam, other molecules giving laser action in the same wavelength range were used.
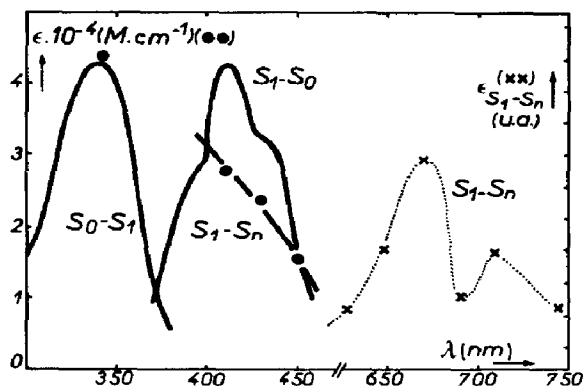
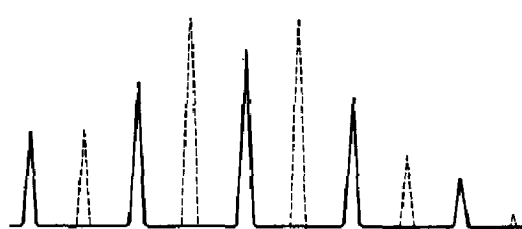Fig. 5. S_1–S_n spectrum of BBO within its fluorescence band and in the visible region.

Fig. 6. Oscillogram of the laser emission of BBO in benzene ($c = 10^{-3}$ M) pumped by the mode-locked ruby laser. Each pulse of the BBO laser emission (dotted line) corresponds to the former pulse of the pumping train (continuous line). It may be seen that the intensity of the BBO laser decreases as the pumping train of pulses travels through the sample, except for the beginning of the train.

For a scintillator solution in benzene (optical density 1 at 3472 Å), the ratio $\alpha_{exp} = T/T_0$ (as defined above) on each pulse of the train was measured as a function of the characteristic wavelength of the probing light. A computer calculation was used to determine the absorption cross section of the first excited singlet state. The two rate equations described above were solved by Hamming's modified predictor/corrector method. Computer solutions give the values of N_0, N_1 and N_T as a function of time from which we obtained the calculated ratio $\alpha_{calc.}$:

$$\log \alpha(t) = l\{(\sigma_e - \sigma_{1n})N_1(t) - \sigma_{TT}N_T(t) - \sigma_{01}N_0 + \sigma_{01}N\}$$

with

$$\alpha_{calc.} = T^{-1} \int \alpha(t)dt$$

On the first pulse of the train, we can disregard the term $\sigma_{TT}N_T(t)$ and the calculated ratio $\alpha^1_{calc.}$ becomes a function of the parameter σ_{1n}. It can be compared with the experimental value α^1_{exp}.

The experimental α^1 values (α^1_{exp}) are reported in Table 4. Computer calculations of α^1, by an interactive method, allow the determination of the best value of σ_{1n} which leads to $\alpha^1_{calc.} \approx \alpha^1_{exp}$. The σ_{1n} values are listed in Table 4. As can be seen, each scintillator, except for the BBOT molecule, presents a high S_1–S_n absorption cross section at the lasing wavelength of the molecule. A typical S_1–S_n spectrum is shown in Fig. 5 for the case of BBO, which shows a substantial absorption of the first excited singlet state in the fluorescence band of the molecule.

In all our experiments, no distortion of the shape of the transmitted train of pulses was observed. This indicates that no build-up of molecules occurs in a transient state absorbing significantly within the laser wavelength range. As a matter of fact, each pulse generates some molecules in the triplet state, according to its own energy; if the next pulse strikes the sample when

the triplet state is not completely relaxed, the triplet population will increase as the excitation train travels through the cell and the transmission of the solution will be reduced. The cross section of the transient then becomes important. Computer calculations of the transmission lead to an upper value of $k_{ST}\sigma_{TT}$ of about 3×10^{-9} s^{-1} cm^{-2} (the term $k_{ST}\sigma_{TT}$ is, to a first approximation, directly proportional to the absorbance of the triplet state).

Discussion

The results of absorption measurements indicate the presence of a triplet state whose kinetic parameters (generation rate constant k_{ST} and lifetime τ_T) have been measured. All the molecules present large triplet–triplet absorptions owing to significant intersystem crossing rates and to high extinction coefficients. When the comparison was possible, the T–T absorption spectra were observed to fit available data concerning PPO [22], BBO [23] and NPO [23].

Two distinct absorptions between the excited singlet states were obtained, one towards the long wavelengths, the other within the fluorescence band. All the molecules investigated exhibited the same behaviour.

These two kinds of transient absorptions must be taken into account to explain the limitation of the lasing performance of scintillators pumped by flashlamp systems. We may describe this problem in a schematic way.

The expression of the gain in a dye laser can be written [7]

$$g(\lambda, t) = \{\sigma_e(\lambda) - \sigma_{1n}(\lambda)\}N_1(t) - \sigma_{TT}(\lambda)N_T(t) - \sigma_{01}(\lambda)N_0(t) - \Omega$$

where Ω is related to the loss of the cavity.

Let us consider a flashlamp excitation whose risetime is t_m. The pumping function is assumed to be linear for $t < t_m$. With $N_0(t) \approx N$ and $N_T \approx (1/2)k_{ST}tN_1(t)$ for $t < t_m$, one obtains

$$g(\lambda, t) = N_1(t) \left\{ \sigma_e(\lambda) - \sigma_1(\lambda) - \frac{1}{2}\sigma_{TT}(\lambda)k_{ST}t - \sigma_{01}(\lambda)\frac{N}{N_1(t)} - \frac{\Omega}{N_1(t)} \right\}$$

The laser effect occurs when $g(\lambda, t) > 0$. In the general case of flashlamp pumped dye lasers (*e.g.* for dye lasers containing coumarins, xanthines or cyanines) σ_{1n} is small and the term $(1/2)\sigma_{TT}(\lambda)k_{ST}$ can be important. As a consequence flashlamps with a risetime of some hundred nanoseconds or more are sufficient to pump the dye. In contrast, scintillators have a high σ_{1n} and the absorption term of the triplet must be as low as possible. As the absorption cross section and the intersystem crossing rate constant are intrinsic parameters of the molecule, one must reduce the risetime of the excitation system. This conclusion corroborates the experimental observations of Furumoto [17] and Maeda [16] who had to develop a flashlamp with a risetime shorter than 80 ns in order to obtain stimulated emission from scintillator molecules.

To show the importance of the triplet absorption, a typical oscillogram of the laser emission of BBO under mode-locked laser pumping is shown in Fig. 6. The laser intensity of the molecule is observed to decrease as the train

TABLE 4

σ_{1n} cross sections in the lasing wavelength range of the molecules

Molecule	Analysing wavelength (nm)	Optical density at 3472 Å	α_{exp}^1	$\sigma_e \times 10^{16}$ (cm^2)	$\sigma_{1n} \times 10^{16}$ (cm^2)
PPO	376	0.8	1.2	1.1	0.9
α-NPO	410	0.8	1.07	0.77	0.6
BBO	410	0.8	1.03	1.6	1.1
PBBO	395	1.0	1.15	1.1	0.9
BBOT	435	1.2	1.32	2.1	1.6
α-NPD	376	1.1	1.05	0.5	0.4
PBD	376	1.1	1.08	1.6	1.5
PPD	376	0.5	1.02	0.55	

of picosecond pulses travels through the sample. This is due to the absorption of the triplet state at the lasing wavelength which becomes more and more substantial because of the accumulation of molecules in this transient state. Thus the gain of the amplifying medium and the laser energy are drastically reduced.

Conclusion

Taking into account the kinetic and spectroscopic parameters of the transient species substantiated by laser spectroscopy, the laser properties of the oxazole and oxadiazole molecules are qualitatively described. The importance of the triplet state is established since this transient appears to be a substantial term in the gain equation which describes the laser emission of scintillators when pumped by flashlamps.

Moreover, this work provides direct evidence for a quenching of the excited singlet state by molecular oxygen, which leads to an enhancement of the singlet–triplet intersystem crossing. This photophysical process is worth investigating by fast spectroscopy since this technique enables us to overcome most of the difficulties generally encountered in steady state investigations.

In addition to this approach to the laser action of these molecules, some original data are reported: transient absorption spectra between excited singlet states, values of extinction coefficients and intersystem crossing rate constants.

Some other points deserve consideration. Several authors have suspected the existence of association between scintillator molecules in solution (*i.e.* dimers and excimers). Owing to the fact that in the case of laser pumped scintillators surprisingly large tuning effects of concentration were observed, such problems of association may reasonably be expected to play an important part in this type of laser pumping. Studies are now in progress to elucidate these points.

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