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The role of the molecular dynamics in the local intensity instabilities of large aperture dye lasers

I. Leyva[a] and J. M. Guerra
Departamento de Óptica, Facultad de Ciencias Físicas Universidad Complutense, Ciudad Universitaria s/n, 28040 Madrid, Spain

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We study experimentally the influence of the molecular dynamics in the local intensity fluctuations of large aperture dye lasers, and find dependencies on solvent viscosity and active molecular size. This is an example of the complexity of the still quite unknown nonlinear processes that underlie the pattern formation dynamics in large aperture optical systems, in which the diffraction has lost influence and the bulk dynamics dominate. © *2000 American Institute of Physics.* [S0003-6951(00)04837-3]

High energy pulsed dye lasers are used in a great deal of practical applications, from isotope enrichment to photodynamic therapy and other scientific or medical uses. To obtain a high power per pulse, these laser systems are designed with increasingly large transversal apertures, in order to obtain more energy when the energy density per area has reached to a limit. However, it has been observed that large transverse dimensions in laser resonators produce complicated spatiotemporal behavior which in some cases affects the practical use. In addition, from a fundamental point of view, the study of such large aperture lasers as pattern forming systems is a difficult task which has generated considerable interest in the last years.

When the system aperture is still relatively small ($F < 10$), its behavior, even if it is irregular, can be explained in terms of modal dynamics. In contrast, for large transverse dimensions, the influence of boundary conditions in the field spatiotemporal dynamics becomes weak. This allows the manifestation of complicated behaviors which are not mediated by diffraction any more, but by bulk mechanisms taking place in the active medium. For instance, this is the case of large aperture systems with optical feedback, whose irregularities suffer the effect of the processes inside the active medium.[1–4]

The nature of those inner bulk mechanisms is not clear in most of the cases. Some theoretical possibilities have been pointed out, as activation–reaction or diffusion[5] in passive systems as optic parametric oscillator (OPO), but so far few experimental works have been devoted to clarify the microscopic structure of these processes. It is clear that the observation of local dynamics in transverse patterns may give significant information about such underlying processes. Pursuing this goal, in this work we show experimental evidence of the importance of the rotational molecular dynamics in the pattern formation process of class A lasers.

In previous experimental works, we observed local irregular intensity fluctuations in a flash-lamp pumped dye laser when the intensity output was measured in small regions of the laser spot (measurement area below 2000 μm^2).[1,3,6] At first sight this fluctuation looks noisy, and so it is confirmed by the single pulse power spectra. However, the power spectra averaged over many shots shows a frequency band peaked around 60 MHz. This peak frequency does not depend on the geometrical characteristics of the resonator, like its length or mirror configuration, neither on the pumping or losses. Thus it seems to be fixed by the intrinsic dynamics of the laser, and quite independent of boundary conditions.

Another important observation is that as the measured area became larger ($1\ mm^2$), the chaotic fluctuation amplitude diminished until it disappears. This extinction happens when the measured area is much smaller that the whole spot ($4000\ mm^2$), and therefore, an interpretation based on transverse mode dynamics can be discarded. This fact indicates the existence of a local chaotic dynamics with a low transverse correlation, whose origin is unknown.

A strong reduction in the amplitude of local irregular fluctuations in a Rhodamine 6G solid copolymer solution has also been observed.[7] That is, the local irregular fluctuations observed in liquid solutions (Rhodamine 6G in methanol), almost disappears in solid solutions. In a recent letter, having ruled out other causes such as thermal effects or dye flux turbulence, we have tested the influence of the solvent viscosity on the fluctuations amplitude. We have observed a monotonous decrease of the relative fluctuations amplitude as the solvent viscosity increases.[8,9] These results suggest an influence of the solvent viscosity on the intensity fluctuations, so it seems that the rotation dynamics of the active centers affects the local irregular dynamics in large Fresnel number dye lasers.

At a microscopic level, the molecules of the amplifying medium interact with the radiation field, which induces a dipolar momentum rigidly bounded to the molecular axis. Hence, a pair of forces acts over the molecule which rotates to align its axis with the field direction. Whenever the host medium in which the molecules are solved happens to be viscous, the angular velocity of this rotation will depend on the viscosity. Since the coupling strength between the induced momentum and the field depend on the angle formed by the molecular axis and the field, it is clear then that there is a relation between the stimulated processes and the solvent viscosity.

Along this line, a semiclassical model to study the ori-

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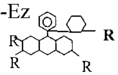
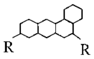
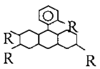
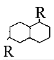
[a] Electronic mail: ileyva@eucmos.sim.ucm.es

TABLE I. Dye features and results for methanol solutions. Molecular sizes calculated by means of the program ChemDPro.

Dye name and structure	Characteristic dimension (Å)	Lasing λ (nm.)	Molecular weight (u.m.a)	Fluctuation amplitude (%)	Fluctuation frequency (MHz.)
Rhodamine Bt-Ez 	19.70	580	614	13 ± 4	~ 45
Violet Cresyl 	14.60	670	362	17 ± 1	~ 50
Rhodamine 6G 	13.90	580	530	21 ± 1	~ 60
Coumarine 504 	7.15	504	313	20 ± 2	~ 80

entational relaxation-dependent spatiotemporal instabilities in high Fresnel number dye lasers has been developed, taking into account the Brownian rotation of excited molecules,[10] which compensates the rotational hole burning. However, this proposed mechanism neglects the fluctuations in the infinite viscosity limit, whereas even in the case of the solid state solution some residual fluctuation are observed experimentally.[9]

In this letter we study experimentally the role of the orientation dynamics of the active centers induced by the field, in the local irregular dynamics of large Fresnel number lasers. All the other previously mentioned experiments, which allow us to relate the fluctuations with the molecular rotation, suggests the study of the influence of those features which are more probable to be involved in the dynamics: the solvent viscosity and the active molecular volume.[7–9] Our aim is to observe how these parameters affect the relative amplitude and frequency of the local intensity fluctuations, in the same way as they were shown to be responsible of other phenomena in dye lasers systems, like lasing anisotropy,[11] laser efficiency,[12] or light polarization.[13]

Our main measurement system consists of a coaxial flash-lamp pumped untuned dye laser having a simple plane-plane resonator. Liquid dye solutions circulate through the flash-lamp inner tube, whose diameter is 18 mm, and the overall discharge length is 320 mm. The laser operates in a single shot regime leaving enough time between two shots to avoid accumulating radial thermal gradients. The solution is changed every one hundred shots, to prevent the effects of dye photolysis. Small areas of the laser beam are selected with two pinholes with diameters of 20 and 30 μm. The light intensity is recorded by means of an optical fiber connected to a photodiode (risetime $\leqslant 1$ ns), linked to a transient programmable digitizer. The whole measurement system is placed inside a Faraday cage to prevent the stray field of the flash-lamp discharge.

In the numerical analysis of the signals, and in order to separate the high frequency fluctuations from the low frequency temporal evolution, we have implemented a high pass mathematical filter with a variable cutoff frequency.[1]

Once the experimental data are filtered by this method, we can concentrate on the study of the frequency of the fluctuations and their relative amplitude percentage (i.e., the ratio between the amplitudes of the high frequency fluctuations and the low frequency temporal evolution). The process has been repeated with a series of pulses (up to 40) in the same experimental conditions and then the results of all individual signals have been averaged.

Two experiments have been carried out. In the first one, the same solvent (methanol), but hosting different dye molecules, allows us to observe the importance of the molecular size and shape in the dynamics. In the second one, the same molecule (Rhodamine 6G), but solved in several polar liquids, give us information about the influence of the viscosity. In all cases, the temperature is fixed to 20 °C.

Our criterion to choose the molecules is to maximize the range of their sizes. Thus, we have chosen Coumarine 504, Rhodamine 6G, Violet Cresyl and another molecule of the Rhodamine family (Rh–BZ–Et), modified to add a very long radical to the basic Rhodamine structure without changing the lasing wavelength.[14] Their structures, lasing wavelength, and sizes can be seen in Table I, as well as the relative fluctuation amplitude and the measured fluctuations frequency. In Fig. 1 we give an example of laser pulses for different dyes [(a) Rh–BZ–Et, and (c) Coumarine 504] and their corresponding power averaged spectra [(b) and (d)]. From this figure it can be appreciated that the pulse for Coumarine 504 shows deeper and faster fluctuations than that for Rh–BZ–Et. Likewise, in the spectra it can be observed that the band has shifted to higher frequencies.

Therefore, the main conclusion to be extracted from these results is that the bigger molecules (Rh–BZ–Et) yield intensity fluctuations with a smaller amplitude and a slower frequency. This result supports the hypothesis of the rotational origin of the effect, which agrees with the fact that bigger molecules have a more difficult movement in their liquid host, and therefore a weaker coupling and nonlinear effect.

Another point to notice is that both kinds of Rhodamine (Rh6G and Rh–BZ–Et), with different size but the same lasing wavelength, yield different results (see Table I), i.e., the lasing wavelength does not seem to play any important role in the effect, which is another evidence to rule out the

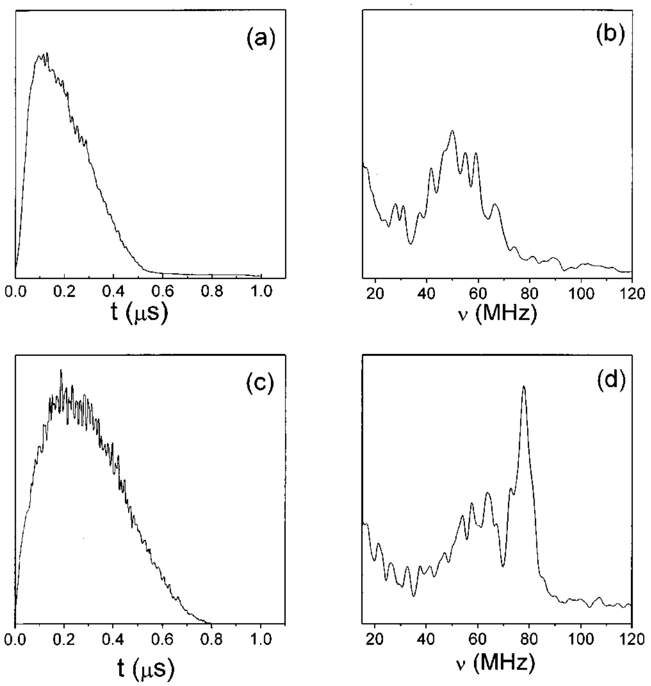


FIG. 1. Experimental intensity pulse using a solution of (a) Rhodamine BZ–Et, (c) Coumarine 504 in methanol. Their corresponding relative fluctuation power spectra, averaged over 40 pulses, for (b) Rh–BZ–Et, (d) Coumarine 504.

importance of the resonator geometry, leaving place only to dynamical interpretations.

For the second experiment, we choose a particular molecule (Rhodamine 6G) and several solvents with different viscosities in order to study its influence on the fluctuations. In order to compare the results obtained with the different solvents, it is necessary to measure them with the same excitation energy, in this case, about 2–3 times over threshold.

An important decrease of the relative fluctuation amplitude percentage as the solvent viscosity increases was previously noticed.[8,9] Now, focusing our attention on the fluctuation frequency, we find that, besides this amplitude loss, there is a reduction in the characteristic frequency. In Fig. 2 we illustrate this effect, showing the normalized power averaged spectra (30 pulses) obtained for the methanol and ethylene glycol solutions ($\eta = 0.6$ and 19.9 cP, respectively). It is clear that the peak has shifted to a lower frequency as the viscosity increases.

Another important piece of information about the dynamics can be extracted from Fig. 2, where it is also shown that the noisy background of the power spectra (apart from the characteristic peak) fits closely to a $a\nu^{-2}$, where $a \simeq 250$ is a fit parameter. This power law is typical of the fluctuation spectra of a zero-dimensional Lorentz system, and different from the expected ν^{-1} law, associated to two-dimensional pattern forming systems with additive noise.[15] However, this feature agrees with a behavior independent of the boundary conditions. In other words, this system, locally, ''forgets'' its bidimensionality and acts as a point-like one. This supports a model of filamented laser emission in which the gain filaments are almost independent of each other.[3]

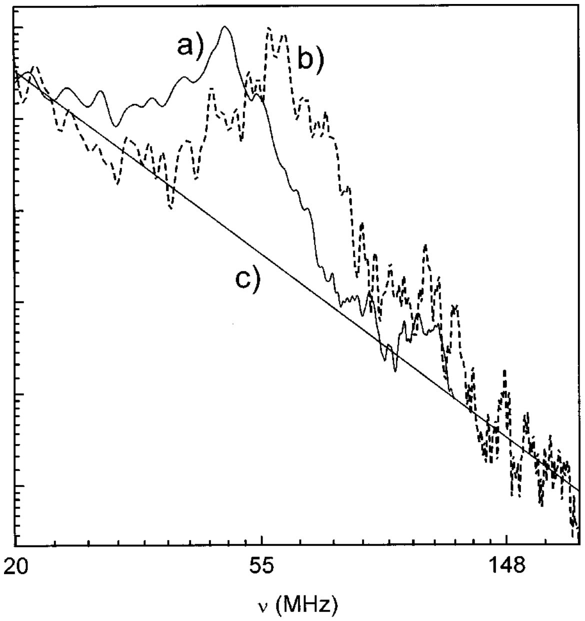


FIG. 2. Log–log plot of the fluctuation power spectra, averaged over 30 pulses for a solution of Rhodamine 6G in: (a) ethylene glycol, $\eta = 0.2$ P. (b) methanol $\eta = 6.0 \times 10^{-3}$ P. (c) Approximate linear fit to $a\nu^{-2}$ of the noisy background, with $a \simeq 250$.

To conclude, in this work we have shown the influence of the molecular dynamics in the local fluctuations of high Fresnel number dye lasers. The reported results highlight the role of the rotational kinetics on the pattern formation process in this kind of laser, which is an example of the complicated and still rather unknown nonlinear interactions that at a deeper level underlie the pattern formation dynamics in large aperture optical systems, in which the diffraction has lost influence and the bulk dynamics dominate.

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