CHANGES IN LASER PULSATION KINETICS DUE TO OPTICAL DAMAGE OF LIQUIDS

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Suspensions of solid, absorbing particles arising when a liquid is damaged by a focused laser beam, are shown to cause an increase or decrease of feedback in pulse lasers: the light undergoes multiple scattering on the absorbing particles and gas bubbles, and the beam in the resonator is diffusionally scattered or diffusionally reflected. The decrease in liquid transparency due to the increase in number of solid particles is evaluated.

Laser pulsations are not, as such, a property of nonlinear effects of stimulated light emission and amplification. Nonetheless, by having recourse to the nonlinear properties of optical effects, the pulsation kinetics can be easily modified. Hitherto the following effects have been described as to their influence on the kinetics of laser pulsations: saturated ebsorption [1–4], nonlinear absorption [5, 6], two-photon absorption [7, 8], perturbation of total internal reflection [9, 10], induced spatial reflection [11–14], stimulated Raman scattering [15], stimulated Rayleigh scattering [16], stimulated Brillouin scattering [17–19], and induced birefringence [20–22]. References to uncited papers are to be found in the monographs [23–28].

We consider the influence of light-induced damage to liquids (LDL), in particular the gradual pyrolysis of benzene, on the kinetics of laser pulsations (LP). The accumulating suspension of carbonized particles (CP) causes fast as well as slow changes in the LP kinetics, simultaneously eliminating all light threshold effects in benzene. On attaining a high CP concentration, the suspension becomes a diffusionally reflecting mirror, whereas the light transmitted forward as a result of scattering on the liquid molecules, CP, and gas bubbles arising in the liquid [29, 30] has but a very slight influence on the LP kinetics. The changes in LP kinetics were studied by comparing the respective emission oscillograms.

We found that the emergence of small numbers of CP in benzene, though undetectable by direct observation of the liquid transparency, modifies characteristically the LP kinetics

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of a ruby laser with plane-confocal resonator, with a 5 cm layer of benzene in its focus. The change consists in a transition from discontinuous emission at high pulsation amplitude to continuous emission with a low amplitude of disordered pulsations (see, Figs 3A2 and 3B2). An increase in CP concentration, e.g. by successive laser flashes, further modifies the LP kinetics (see, Figs 3A1 to 3H1). In the case of an Nd-laser, the CP effect was similar, although pure benzene, by its 8300 cm^{-1} absorption band [31], suffices to affect the LP kinetics by absorption of the Nd-laser wave $\lambda = 1.06$ μm (see, Figs 3A to 3H).

Benzene, when in the focused beam of an Nd or ruby laser of output power upwards of several kW per cm^2, easily goes over into a strongly light scattering suspension of carbonized particles. The mechanism leading to CP formation is not known in detail. Nonetheless, lateral pictures of the beam in the liquid, emission oscillograms, and transparency observations all suggest that various products, namely gaseous hydrogen and light hydrocarbons, liquid aromatic hydrocarbons as well as solid carbonized particles arise in the region of the beam focus. On filtration of the suspension a soot-like residue is obtained. Observation of the liquid after successive laser shots shows that the carbonized particles increase in size e.g. as a result of nucleation, and fall to the bottom of the cuvette with the suspension.

It is possible to follow theoretically the changes in transmission of the benzene layer in the focus due to the production of CP. The number of originally formed CP is dependent on the temperature of the benzene. If one carbonized particle arises by chemical bonding of b benzene molecules e.g. in a reaction of the type

$$b\mathrm{B} \xrightarrow{k} \mathrm{C}, \tag{1}$$

we have

$$dc_C/dt = -(1/b)\,(dc_B/dt) = kc_B, \tag{2}$$

with k — the rate constant of the reaction given as

$$k = A \exp(-E/RT), \tag{3}$$

c_B the concentration of benzene molecules, and c_C that of carbonized particles in moles per litre. Integration of (2) leads to

$$c_C(t) = c_C(0) + (c_B(0)/b)\,[1 - \exp(-kbt)] \cong c_C(0) + c_B(0)kt/(1+kbt). \tag{4}$$

Hence, in order to determine the concentration of carbonized particles at an arbitrary moment of time t we have to have available the reaction rate k as a function of time. In fact, differentiating Eq. (3) we obtain

$$dk = (R/E)[\ln(k/A)]^2 kdT. \tag{5}$$

The temperature of the benzene layer in the focus increases with time t according to the equation

$$dT = (1/VC_v)\,(\partial Q/\partial t)_{t=\mathrm{const}} dt \tag{6}$$

whereas

$$(\partial Q/\partial t)_{I=\text{const}} = S\Delta I = I_0 - I_0 \exp\{-\varepsilon l[c_C(0)+c_B(0)kt/(1+bkt)]\}.$$

On insertion of (6) into Eq. (5), series expansion of the exponential function, and putting $c_B(0)kt/(1+bkt) = 0$ we obtain

$$k = A \exp\{(-E/R)[1/(T_0+\alpha I_0 t)]\}, \tag{7}$$

whereas

$$\alpha = c_C(0)/C_v[1+\varepsilon l c_C(0)].$$

Hence the transmission of the suspension at the moment of time t, on neglecting scattering, amounts to

$$\mathcal{T} = I/I_0 = \exp\{-l\varepsilon[c_C(0)+c_B(0)k_a t/(1+k_a bt)]\}, \tag{8}$$

where

$$k_a = (1/t)\int_0^t k\,dt,$$

and k is given by (7). Eq. (8) is plotted in Fig. 1 for the following numerical values: length of focus cylinder $l = 0.5$ cm, laser action duration $t = 200$ μs, molar absorption coefficient $\varepsilon = 10^4$ litre/mole cm, activation energy $E = 5.10^4$ cal, constant A of Eq. (3) equal to

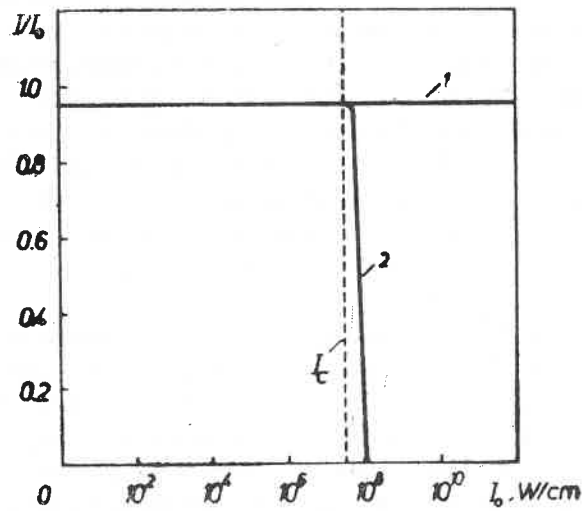

Fig. 1. Laser beam power losses in a benzene layer, containing a suspension of carbonized particles of increasing concentration. The curves *1* and *2* represent transmission through the benzene layer with constant number and with increasing number of the absorbing particles respectively. I_C denotes the laser beam intensity necessary to pyrolyse the liquid benzene

10^{12} sec^{-1}, specific heat of the suspension at constant volume $C_v = 1.5$ J cm^{-3} deg^{-1}, initial concentration of benzene molecules $c_B(0) = 11.2$ mole/litre, that of carbonized particles $c_C(0) = 10^{-5}$ mole/litre, and initial temperature of the suspension $T_0 = 295$ K. Fig. 1 shows that upwards of the intensity I_C of the incident beam that of the emergent beam decreases steeply. Thus, the CP suspension in benzene acts as an optical amplitude limiter,

forbidding the transmission of beams of high intensity. At incident intensities less than I_C, the fundamental process consists in multiple scattering of light on the CP. The strong scattering causes a smoothing of the excitation conditions for many axial as well as non-axial modes apparent as a smoothing of pulsation in the laser pulse. However, with increasing CP concentration, the number of modes excited undergoes a considerable limitation; then, phase synchronisation of the modes and regular laser pulsation take place (Figs 3G2, 3H2). A further increase in CP concentration does not cause laser action to vanish since the suspension becomes a diffusionally reflecting mirror. The condition for the production of CP resides in the presence of some absorption in the benzene; usually, this is ensured by small dust particles, suspended in the liquid. If carefully filtered benzene is used (which is known [15] to cause an increase rather than a smoothing of pulsations) the addition of several drops of benzene preliminarily subjected to dielectric breakdown suffices to initiate the process of CP production. With a wave of $\lambda = 1060$ nm this is unnecessary. The effect of breakdown and the ensuing increase in scattering of the focused beam in benzene are shown in Fig. 2.

To study the influence of LDL on the pulsation kinetics, we used the laser setup with plane-confocal resonator described in Ref. [32, 33] with the parameters: ruby rod $\varnothing = 10$ mm, $l = 100$ mm, or Nd-glass rod $\varnothing = 10$ mm, $l = 130$ mm; mirrors $T_1 \cong 35\%$, $T_2 \cong 0\%$; achromatic lenses $f_1 = f_2 = 150$ mm confocally inserted between T_1 and the rod; thermostatized cuvette with benzene $l = 50$ mm in the focus of the lenses. The setup provided an almost arbitrary radiation field density in the liquid, simultaneously preserving density and parallel symmetry of the field in the lasing medium, and was insensitive to slight changes of the inter-lens distance. These performances recommended it for the present work and for studies of nonlinear optical effects in liquids [15, 18].

Fig. 3 shows the effect of LDL on LP kinetics. The series of oscillograms A1–H1 and A2–H2 are for laser emissions with a ruby rod, whereas A–H is for an Nd rod. For each oscillogram the pumping energy of the lasing rod is given.

The series A1–H1 shows slow changes in LP kinetics due to CP concentrations in benzene increasing under the action of the laser beam. The formation of CP lowers the intensity of the transmitted beam and raises that of the reflected beam. For A1–F1 transmission predominates, whereas in the cases of G1, H1 — reflection. After Ref. [33], we assume that the maximal reflected intensity does not exceed $0.5\, I_0$.

The series A2–H2 shows three extremal cases. A2 and B2 show the rapid change in emission kinetics when several drops of a CP suspension are added to benzene, A2 relating to pure benzene and B2 to the same benzene on addition of the suspension. After some 10–20 laser flashes (selected ones are shown in C2–F2, amplification twice enlarged) emission takes the shape shown in G2 and H2. The oscillograms G2 and H2 visualize the growth of laser pulsations due to multiple scattering and phase synchronisation of the modes, with beam focusing occuring along the symmetry axis of the rod.

The series B–H shows the influence of absorption in pure benzene on the laser emission kinetics of the Nd setup. The introduction of pure benzene into the ruby setup causes no such effect. Oscillogram A shows the emission of an Nd-laser with a plane resonator, of a length equal to that of the laser setup applied.

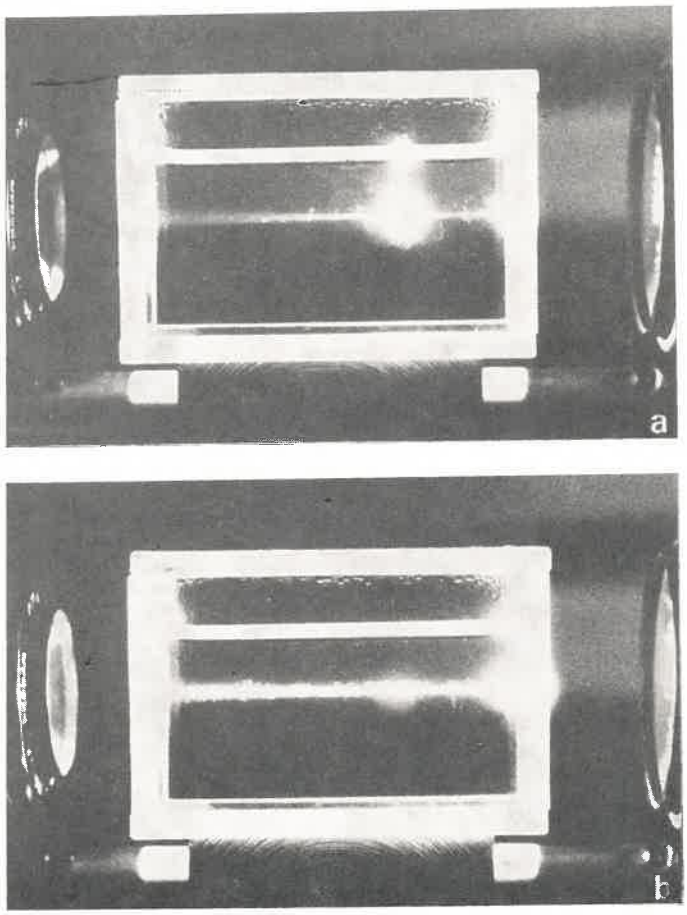

Fig. 2. Phenomenon of laser beam scattering in cuvette with benzene in the centre of a co-focal system of lenses in the cavity of a ruby laser. The pictures show two successive laser shots: (a) dielectric breakdown, involving small dust particles present in the chemically pure benzene, (b) scattering of the laser beam on carbonized particles, produced in the breakdown process, and on small gas bubbles. The shutter was kept open throughout the laser action

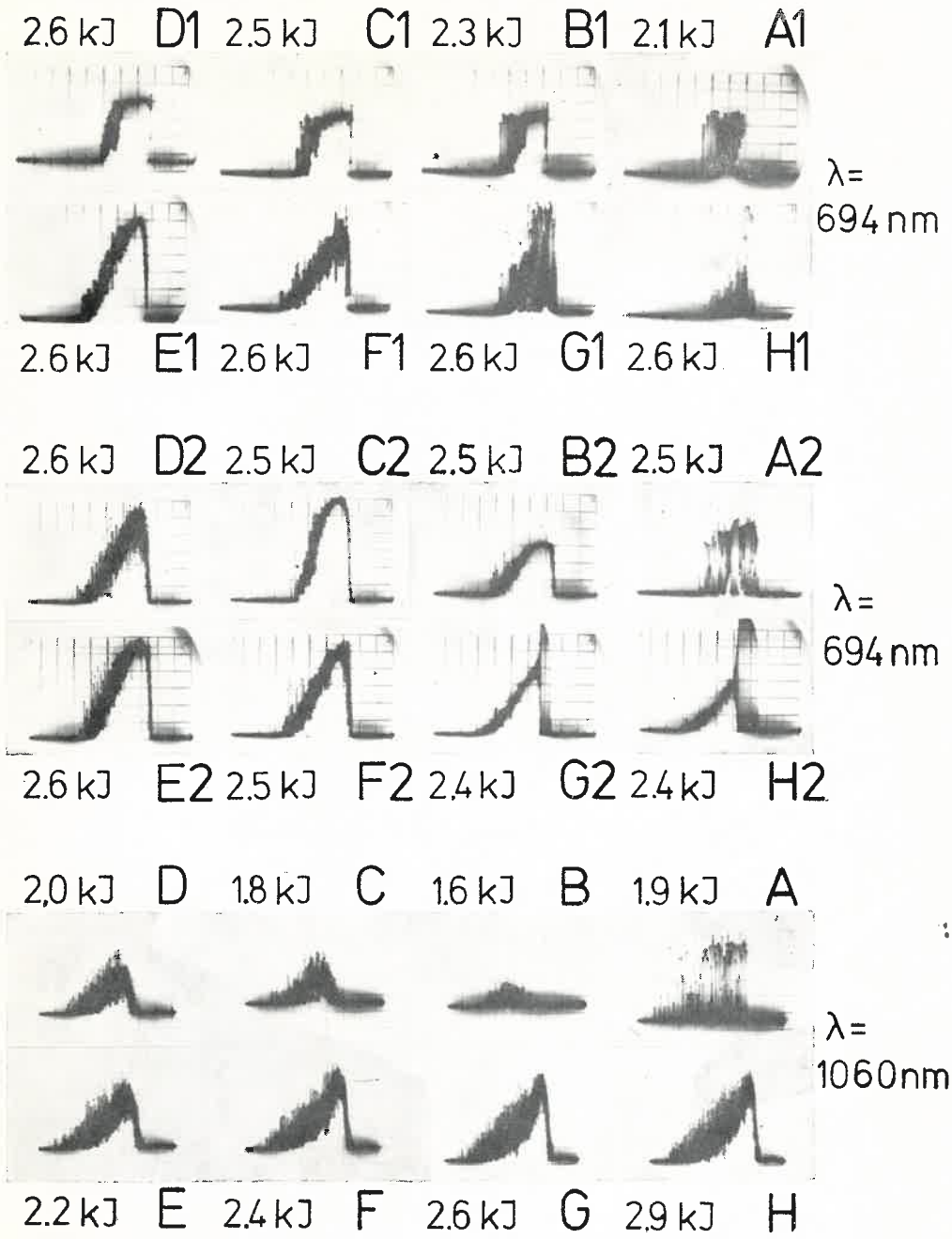

Fig. 3. Pulsations in emission of a laser with, in the focus of plane-confocal resonator, a transparent liquid undergoing damage as the result of intense illumination. The series of oscillograms A1–H1 and A2–H2 show the effect on the kinetics of emission pulsation of a ruby laser caused by the production of carbonized particles in benzene. The series A–H visualizes the influence of pure benzene on the emission pulsation kinetics of a neodymium laser

Generally, the present work provides the first determinations of the changes in ruby and Nd-laser pulsation kinetics due to damage of liquid by laser action. Moreover, further details concerning the mechanism of LP production and the process of benzene pyrolysis are presented.

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