A Criterion for Probable Laser Quenching

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An analytic criterion is proposed for assessing the moment of laser quenching, power of generation, and the energy of stimulated emission for alkyl iodide photodissociation lasers with an unknown mechanism of accumulation of molecular iodine. The criterion is equivalent to the statement that four photolysis acts are accompanied by the formation of a single iodine molecule and correspond to maximum quenching rate.

THE reason for the quenching of photodissociation lasers based on alkyls and perfluoroalkyls of iodine mixed with a buffer gas is customarily believed[1-3] to be deactivation of the excited iodine atoms by the iodine molecules in the quenching reaction

$$I(^2P_{1/2}) + I_2 \xrightarrow{k_q} I(^2P_{3/2}) + I_2. \tag{1}$$

If this model is assumed, then the rate of the quenching processes is determined by the concentration of the molecular iodine, the accumulation of which cannot be described analytically even in the simplest case of a pure recombination mechanism.[1]

It is therefore useful to present an analytic estimate of the power, instant of quenching, and output energy of the stimulated emission by starting from the assumption that the deactivation processes proceed at the maximum rate permissible by the conservation laws. The ensuing quantitative results give minimal values for the parameters indicated above. If we assume in addition that all the possible values of the molecular-iodine concentration are equally probable, then it turns out that the exact values of the parameters of the kinetic calculations differ little, with overwhelming probability, from the analytical estimates.

An expression for the stimulated-emission power W(t) from a unit volume of the working medium can be obtained from the condition that the population difference between the excited and ground levels $^2P_{1/2}$ and $^2P_{3/2}$ of the atomic iodine be stationary during the lasing regime. The inversion[1)]

$$\Delta = [I(^2P_{1/2})] - 0.5[I(^2P_{3/2})] \tag{2}$$

is maintained constant and equal to the threshold value Δ_{thr} by simultaneous action of the following processes: 1) pumping of the iodine atoms to the upper level $^2P_{1/2}$ as a result of photodissociation of the working-medium molecules at a rate $k_p(t)[RI]$; 2) stimulated transitions between the levels $^2P_{1/2}$ and $^2P_{3/2}$ with a rate $-1.5W(t)/h\nu$; 3) quenching of the excited atoms at a rate $-1.5k_q[I(^2P_{1/2})][I_2]$. Here $k_p(t)$ is the rate constant of the photodissociation reaction of the molecules of the working medium RI, $h\nu$ is the energy of the stimulated-emission quantum, and k_q is the rate constant of the reaction (1).

In photodissociation lasers, $\Delta_{thr} \ll [I]$, and when allowance is made for the double degeneracy of the ground level, one-third of the total number of atoms is at the $^2P_{1/2}$ level. Setting up a balance of the rates of all the processes that maintain the stationary inversion, we obtain an expression for the specific radiation power

$$W(t) = {}^2/_3 h\nu\{k_p(t)[RI(t)] - 0.5k_q[I(t)][I_2(t)]\}, \tag{3}$$

where $[I] \equiv [I(^2P_{1/2})] + [I(^2P_{3/2})]$.

It follows from (3) that generation continues until the pumping rate $k_p(t)$ [RI] exceeds the quenching rate $0.5k_q[I][I_2]$, and equality of these quantities

$$k_p(t)[RI] = 0.5k_q[I][I_2] \tag{4}$$

determines the instant t_q of laser quenching. The solution of (4), i.e., the instant of time t_q, depends on the mechanism whereby the molecular iodine is accumulated. Therefore the connection between t_q and the remaining parameters of the problem cannot be obtained in the general case. It is easy, however, to obtain an analytic expression for the instant of time t*, defined such that prior to t* laser quenching is completely impossible for any mechanism of molecular-iodine accumulation. The quantities [I(t)] and $[I_2(t)]$ which enter in (3) and (4) are not independent by virtue of the conservation of the number of iodine atoms:

$$[I(t)] + 2[I_2(t)] = n(t), \tag{5}$$

where $n(t) = [RI(t=0)] - [RI(r)]$ is the number of working-medium molecules that have decomposed by the instant of time t. Therefore the instantaneous value of the quenching rate

$$0.5k_q[I][I_2] = 0.5k_q\{n(t) - 2[I_2]\}[I_2]$$

depends quadratically on the concentration of the molecular iodine at this instant of time and reaches a maximum at $[I_2] = 0.25n$ or $[I] = 0.5n$. The maximum quenching rate is $k_q n^2(t)/16$. Thus, the quenching is most effective when half of the iodine atoms released as a result of the photolysis are bound into molecules. If the pumping rate exceeds the maximum possible quenching rate,

$$k_q(t)[RI] > {}^1/_{16}k_q\{[RI(0)] - [RI(t)]\}^2, \tag{6}$$

then the laser quenching is certainly impossible. Laser quenching becomes possible in principle only if the inequality (6) is not satisfied, when the pumping rate does

1)The square brackets, as usual, denote the concentration of the substance.

not exceed the maximum possible quenching rate. The equality

$$k_p(t)\,[\mathrm{RI}(t)] = {}^1/_{16}k_q\{[\mathrm{RI}(0)] - [\mathrm{RI}(t)]\}^2 \qquad (7)$$

determines the characteristic instant of time t*, starting with which laser quenching becomes possible in principle. By the same token, the solution of (7), in the sense of determining the instant of time t*, gives a lower bound for the quenching instants, $t^* \leq t_q$. Equation (7), unlike (4), contains quantities that can easily be calculated analytically and do not depend on the mechanism whereby the molecular iodine is accumulated.

It is important to note that t* is determined only by the known[4] rate constant of the quenching reaction (1) and by the pump photon flux density $I_\nu[T(t)]$, which enters in the structure of the constant $k_p(t)$:

$$k_p(t) = \int\limits_0^\infty \sigma(\nu) I_\nu[T(t)]\,d\nu, \qquad (8)$$

where $\sigma(\nu)$ is the effective cross section for the absorption of the medium RI and T is the temperature of the pump source.

If the real quenching rate is replaced in (3) by the maximum value, we obtain a lower bound of the specific radiation power

$$W(t) \geqslant W^*(t) = \frac{2}{3}h\nu\left\{k_p[\mathrm{RI}] - \frac{k_\tau}{16}n^2(t)\right\}, \qquad (9)$$

and also a lower estimate for the total yield of the generation energy

$$E = \int\limits_0^{t_q} W(t)\,dt \geqslant E^* = \frac{2}{3}h\nu\left\{n(t^*) - \frac{k_\tau}{16}\int\limits_0^{t^*} n^2(t)\,dt\right\}, \qquad (10)$$

with

$$n(t) = [\mathrm{RI}(0)]\left(1 - \exp\left\{-\int\limits_0^t k_p(t)\,dt\right\}\right). \qquad (11)$$

Let us consider as an example a pump pulse of rectangular form, $k_p(t) = k_p$ = const. In this case the decomposition of the medium is exponential and

$$n(t) = [\mathrm{RI}(0)](1 - \exp\{-k_p t\})$$

Introducing the notation $B = k_p/k_q[\mathrm{RI}(0)]$, the quenching criterion (7) takes the form

$$\exp\{k_q t^*\} = 1 + 8B + \sqrt{16B + 64B^2}. \qquad (12)$$

It is easy to verify that $8B \ll 1$ in the case when the pumping is by flash lamps and under ordinary conditions of filling of the cell with the working medium; the criterion (12) then takes the simpler form $\exp(k_p t^*) = 1 + 4\sqrt{B}$, and

$$t^* = 4/\sqrt{k_p k_q[\mathrm{RI}(0)]}. \qquad (13)$$

This relation agrees with the experimentally observed decrease of the laser generation time with increasing pump-pulse power or with increasing initial concentration of the working medium. In the same approximation, we find that the laser emission power should be no less than

$$W^*(t) = \frac{2}{3}h\nu k_p[\mathrm{RI}(0)]\left\{1 - \left(\frac{t}{t^*}\right)^2\right\},$$

and the energy drawn from unit volume should exceed the quantity

$$E^* = {}^{16}/_9 h\nu\sqrt{k_p[\mathrm{RI}(0)]/k_q} \qquad (14)$$

i.e., in spite of the fact that the generation time decreases with increasing product $k_p[\mathrm{RI}(0)]$, in accordance with (13), the specific energy yield increases in accordance with (14).

Let us compare the estimate (7) of the instant of laser quenching with its exact value obtained from a numerical calculation for the recombination mechanism of molecular-iodine accumulation. Figure 1 shows the results of a kinetic calculation, taken from the paper of Zalesskiĭ and Vendediktov.[1]

The last column of the table gives the results of an estimate, in accordance with formula (7), at the pump-pulse intensity indicated in [4] (curve 4, Fig. 1). It is of interest to explain the somewhat surprising effectiveness of a quenching criterion based on a rather crude assumption concerning the maximum rate of the quenching processes. To this end we present a quantitative probabilistic estimate of the effectiveness of the quenching criterion.

Since we do not know the time variation of the I_2 concentration in (3), it is convenient to regard the power as a function of two independent variables, the time and the molecular iodine concentration, $W = W(t, [I_2])$. As a result of the conservation law (5), the value of $[I_2]$ at any fixed t can range from 0 to 0.5n(t), and the relation $W = W([I_2])$ is quadratic. The roots of the $W([I_2])$ parabola, i.e., the solutions of the equation $W([I_2]) = 0$, are

$$[I_2(t)]_{1,2} = \frac{n(t)}{4}\left\{1 \pm \sqrt{1 - 16\frac{k_p[\mathrm{RI}(t)]}{k_q n^2(t)}}\right\}, \qquad (15)$$

and consequently there are no real (and positive) values of the concentration $[I_2]$, corresponding to the case $W = 0$, until the radicand in (15) becomes equal to zero. At all earlier instants of time we have $W(t) > 0$ for all permissible values of $[I_2]$, and laser quenching is impossible regardless of the mechanism whereby the molecular iodine is accumulated. At t = t* there appears on the $(t, [I_2])$ plane a region $W < 0$, shown in Fig. 2, which broadens with increasing time, gradually filling the entire interval (0, 0.5n(t)) of the possible I_2 concentration values. The limits of the quenching region $W < 0$ are the roots of (15),

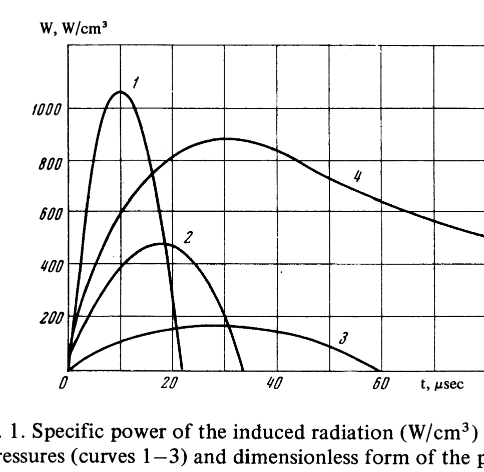

FIG. 1. Specific power of the induced radiation (W/cm³) for different initial pressures (curves 1–3) and dimensionless form of the pump pulse (curve 4) as functions of the time.

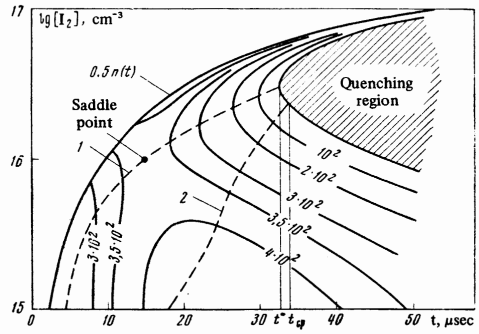

FIG. 2. Curves of equal specific power on the (t, $[I_2]$) plane and the quenching region $W < 0$ for the case of curve 2 of Fig. 1. The dashed curves correspond to different mechanisms of production of molecular iodine: 1—mechanism leading to the maximum quenching rate, 2—recombination production mechanism.

and with increasing t the larger of the roots tends to 0.5n(t) and the smaller one to zero. The solid curves in Fig. 2 are constant-level lines of the surface $W(t, [I_2])$, corresponding to a concrete set of initial data—the case of curve 2 in Fig. 1. The dashed line 2 shows the accumulation of the molecular iodine $[I_2(t)]$ via the recombination mechanism proposed in the calculation of curve 2 of Fig. 1 in [1]. The lasing pulse for this case $W(t) = W(t, [I_2(t)])$ corresponds to the cross section of the surface $W(t, [I_2])$ on Fig. 2 along the curve for the recombination production of the iodine $[I_2(t)]$. The molecular-iodine accumulation curve corresponding to the case of maximum quenching rate

$$[J_2(t)]_{\text{max. q.}} = {}^1/_4 n(t)$$

passes through the saddle point of the surface $W(t, I_2)$ and falls in the region $W < 0$ at $t = t^*$. Graphically, the instant t^* corresponds to the instant of appearance of the region $W < 0$, and t_q represents the instant when the $[I_2(t)]$ curve enters this region. If, after it comes into being, the "quenching region" expands quite rapidly, the values of t^* and t_q certainly differ little from each other, so that the proposed estimate is accurate. Let us determine the rate of expansion of the quenching region for a constant-intensity pump source. Substituting in (15) the expressions for $[RI(t)]$ and n(t), and using (13), we can obtain the form of the boundary of the quenching region:

$$[I_2(t)]_{1,2} = {}^1/_4 n(t)\ \{1 \pm \sqrt{1-(t^*/t)^2}\}. \tag{16}$$

A quantitative measure of the effectiveness of the

Number of curve	Initial density, cm⁻³	Calculated quenching time, μsec	Estimated from quenching criterion, μsec
1	$1\cdot10^{19}$	22	22
2	$3.3\cdot10^{18}$	34	33
3	$1\cdot10^{18}$	60	52

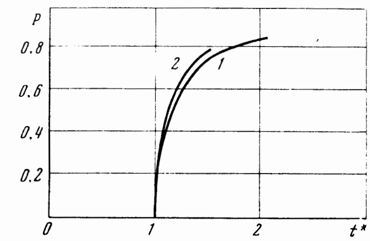

FIG. 3. Probability of absence of generation as a function of the time in units of t^* for constant pump power (1) and for a pump pulse having the shape of curve 4 of Fig. 1 (2).

quenching criterion can be obtained by assuming that at each instant of time all the permissible values of the I_2 concentration are equally probable. Then the probability of absence of lasing at the instant t will equal the ratio of the width of the quenching region at this instant to the quantity 0.5n(t), which determines the range of possible values of the I_2 concentration. For a constant-intensity pump source, the probability P(t) that there is no generation at the instant t is equal to the difference between the roots (16) divided by the range of possible concentration values

$$P(t) = \frac{[I_2(t)]_1 - [I_2(t)]_2}{0.5n(t)} = \sqrt{1-(t^*/t)^2}.$$

A plot of P(t) is given by curve 1 of Fig. 3 and shows that the probability of absence of generation becomes appreciable already for a 15% lengthening of the quenching time in accordance with the criterion $P(1.15t^*) = 0.5$, and is close to unity for double the criterial time $P(2t^*) = 0.85$. The effectiveness of the criterion depends little on the shape of the pump pulse, as can be readily seen by comparison with curve 2 for P(t), calculated for a pump pulse having the time dependence represented by curve 4 of Fig. 1.

The quenching criterion proposed by us corresponds to the case when there is no information whatever on the mechanism of molecular-iodine accumulation. Any reliable information on the accumulation mechanism can be used to improve this criterion.

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