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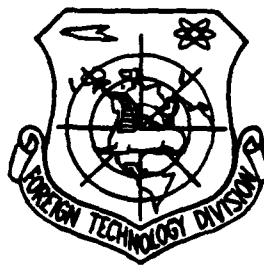
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# FOREIGN TECHNOLOGY DIVISION



UKRAINIAN PHYSICS JOURNAL  
(Selected Articles)



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U. S. BOARD ON GEOGRAPHIC NAMES transliteration SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

\*ye initially, after vowels, and after ъ, ь; e elsewhere.  
When written as ѣ in Russian, transliterate as yĕ or ě.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh <sup>-1</sup>
cos	cos	ch	cosh	arc ch	cosh <sup>-1</sup>
tg	tan	th	tanh	arc th	tanh <sup>-1</sup>
ctg	cot	cth	coth	arc cth	coth <sup>-1</sup>
sec	sec	sch	sech	arc sch	sech <sup>-1</sup>
cosec	csc	csch	csch	arc csch	csch <sup>-1</sup>

Russian English

rot curl  
lg log

GRAPHICS DISCLAIMER

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KINETICS OF LASERS BASED ON LIGHT-INDUCED CHEMICAL REACTION IN  
STATIONARY REGIME

V. A. Kochelap, S. I. Pekar

The theory of the stationary regime is developed for a laser based on light-induced chemical reaction. The threshold conditions are obtained for generation arising, the quantum yield investigated as dependent on pumping power.

The reactions of the addition and exchange (or substitution) type are considered separately.

The theory contains the kinetics of an «ordinary» chemical laser as a limiting case.

### Introduction

At the present time interest is growing in lasers, in which the energy of exothermic chemical reactions is used [1-8]. In such lasers usually the process can be divided into two stages: 1) occurring without the participation of light of the chemical reaction, the products of which are excited molecules; 2) induced radiation of excited molecules, taking place without chemical reaction. The first stage is an ordinary chemical reaction and its rate can limit the

speed and the power of the entire laser process. The second stage so far was possible to accomplish only in gas with rather low pressure, since the excited molecule should manage to emit light before it is deactivated during collision with other molecules. Limitation of pressure also leads to limitation of the power of light emission.

One of the authors [9] proposed another type of chemical laser, in which the induced phototransition of electrons is accomplished at the moment of contact of unexcited gas molecules and coincides with the elementary act of the chemical reaction. In this case with the growth of radiation intensity, not only the induced phototransitions are accelerated, but to the same extent the chemical reaction itself. The last, therefore, is not the factor limiting the speed and power of the laser process.

In works [9-11] was calculated the amplification factor of light in a mixture of gases, consisting of unexcited molecules, between which occurs the exothermic reaction. Amplification turned out to be (with the appropriate selection of substances) fully adequate for creation of the laser.

In this article is examined the kinetics of the chemical laser proposed in [9] in stationary regime, with uniform in space (not depending on coordinates) density of pumping power, radiation

intensity, concentrations of initial molecules and reaction products in supermode approximation. Below the calculations will be produced for two cases: reactions of the recombination or addition type, when the product of the elementary act of the reaction is one molecule, and reactions of exchange or substitution type, with which two unconnected molecules appear.

#### Addition reactions.

Let us assume the reaction equation has the form  $A+B=AB$ . Let us assume that during the reaction the concentrations of molecules A and B remain identical  $n_A=n_B=n$ . Let us assume  $m$  - concentration of molecules AB. Two ways of appearance of contacting molecules A and B are possible. a) Simple elastic gas-kinetic collision, with which the time of contact is on the order of  $10^{-13}$  s. This is usually realized in the case of simple monatomic molecules. b) Gas-kinetic collision, with which the kinetic energy of relative motion of two molecules first changes into energy of internal degrees of freedom of these molecules, as a result of which they turn out to be connected for a longer time. In the formed quasi-molecule the atoms accomplish conservative motion until at the degree of freedom, corresponding to relative motion, is fluctuatingly concentrated the energy, sufficient for dissociation of the quasi-molecule again on A and B. The approaching molecules A and B, as is known, can form a quasi-molecule

radiated photons into the working mode, i.e., number of phototransformations of quasi-molecules, located in the first electron state, into reaction products (stable molecules AB);  $a_{qm}$  - number of opposite phototransitions;  $k'n'$  and  $k''n''$  - numbers of elementary acts of chemical reaction, accomplished by other mechanisms (ordinary thermal chemical reaction, radiation chemical reaction with spontaneous radiation of photons, not belonging to working mode);  $g_{1,m}$  and  $g_{2,m^2}$  - speeds of removal of reaction products (linear and quadratic in concentration),  $\gamma_q$  - speed of escape of photons of working mode referred to a unit of volume: scattering of photons in the volume, incomplete reflection by mirrors etc.

It should be emphasized that the speeds of ordinary thermal chemical reactions can be determined by collisions of quasi-molecules with third bodies (initial molecules, reaction products, molecules of extraneous gas). Therefore coefficients  $k'$  and  $k''$  can depend on the concentration of these bodies. The remaining coefficients  $r'$ ,  $r''$ ,  $d'$ ,  $d''$ ,  $g_1$ ,  $g_2$ ,  $a$ ,  $a''$ ,  $b$ ,  $\gamma$  do not depend on the concentration, but depend on the temperature, if we assume that for each electron state of molecules and quasi-molecules there is successfully established thermal equilibrium with respect to oscillatory, rotational and forward degrees of freedom with the same temperature. If such thermal equilibrium is not successfully established, then the mentioned coefficients will depend on the speed of the entire laser process,

in several electron states. Let us assume for simplicity that subsequently only two of such electron states play the main role,  $n'$ ,  $n''$  - concentrations of quasi-molecules in these states.

Let us formulate the kinetic equations for case b). As a particular case, case a) will be contained in them. If  $q$  - concentration of photons of working mode,  $V$  - volume of resonator, then the kinetic equations can be written in the form

$$\frac{dn}{dt} = W - (r' + r'')n^2 + d'n' + d''n'' + a'n''q = 0, \quad (1)$$

$$\frac{dn'}{dt} = r'n^2 - (d' + k')n' - b\left(\frac{1}{V} + q\right)n' + aqm = 0, \quad (2)$$

$$\frac{dn''}{dt} = r'n^2 - (d'' + k'' + a''q)n'' = 0, \quad (3)$$

$$\frac{dm}{dt} = b\left(\frac{1}{V} + q\right)n' - aqm + k'n' + k''n'' - g_1m - g_2m^2 = 0, \quad (4)$$

$$\frac{dq}{dt} = b\left(\frac{1}{V} + q\right)n' - aqm - a''qn'' - \gamma q = 0. \quad (5)$$

Here  $W$  - pumping power density, i.e., number of pairs of initial molecules A and B, entering a unit of volume per second;  $r'n^2$  and  $r''n^2$  - numbers of recombinations of molecules A and B in a unit of volume per second with the formation of quasi-molecules in the first and second electron states;  $d'n'$  and  $d''n''$  - numbers of thermal dissociations of these quasi-molecules on molecules A and B,  $a''qn''$  - number of absorbed photons by quasi-molecules in the second electron state, where absorption is accompanied by dissociation of quasi-molecule;  $b(1/V+q)n'$  - number of spontaneously and inducedly

i.e., on  $W$ . The last four of the mentioned coefficients depend also on the frequency of photons of the working mode.

It should be emphasized that equations (1)-(5) can describe the kinetics also of an ordinary chemical laser (see, for example, [4]), in which the elementary act of the chemical reaction of addition, with the formation of stable excited molecule, precedes the act of induced radiation. In this case term  $r'n^2$  should be interpreted as the rate of the chemical reaction with the formation of molecule  $AB$  in the excited electron state, from which induced phototransition is accomplished. Term  $r''n^2$  corresponds to the chemical reaction with the formation of the same product, but in another electron state. Coefficients  $d'$  and  $d''$  should be assumed equal to zero, which corresponds to disregarding of the reverse chemical processes. Coefficient  $a''$  also should be assumed equal to zero. Terms  $k'n'$  and  $k''n''$  should be interpreted as the speeds of deactivation of excited reaction products.

It is obvious that term  $r''n^2$ , as term  $k'n'$ , corresponds to the process, reducing the quantum yield of the laser. For simplicity let us first drop these terms, i.e., let us examine a laser with quantum yield equal to one. In this case the number of photons radiated by the laser, referred to a unit of volume of gas, in a unit of time is equal to  $W$ . Let us clarify in what cases in the stationary regime

that  $W$  can be large.

From (1) we see that  $W \leq r'n^2$ . Consequently, large laser power in principle is connected with large value of  $r'$  and high gas pressure. In this connection it is interesting to compare the possibilities of an ordinary chemical laser and the laser examined in [9]. For the ordinary chemical reaction of addition, being accomplished with three collisions of molecules,  $r'_{\text{chem}} \leq uv^2 n_3$ , where  $v$  - gas-kinetic volume of molecule,  $u$  - its average thermal rate,  $n_3$  - concentration of molecules, being the "third body". However, in the laser examined in [9],  $r'n^2$  - number of simple gas-kinetic paired collisions in a unit of volume per second, so that  $r' = uv^2$ . Thus,

$$\frac{r'_{\text{chem}}}{r'} \leq 0n_3. \quad (6)$$

With  $v = 10^{-23}$  cm<sup>3</sup> and  $n_3 = 10^{19}$  cm<sup>-3</sup>  $\frac{r'_{\text{chem}}}{r'} \leq 10^{-4}$ . Consequently, the principle power limit of the laser, examined in [9], considerably exceeds the power limit of ordinary chemical lasers.

Returning to the solution of system of equations (1)-(5) with terms  $r'n^2$  and  $k'n'$ , let us eliminate from them  $n$ ,  $n'$  and  $n''$ , having expressed them through  $q$  and  $m$ :

$$n^2 = \frac{d'' + k'' + \alpha'' q}{r''} n', \quad (7)$$

$$n' = q \frac{(am + \gamma) \left(1 + \frac{r' b_0}{r'' d'} q\right) + b_0 \frac{W}{d'}}{b \left(\frac{1}{V} + q\right) \left(1 + \frac{r' b_0}{r'' d'} q\right) - b_0 q}, \quad (8)$$

$$n'' = \frac{b_0}{\alpha''} \frac{(am + \gamma) q + \frac{W}{d'} b \left(\frac{1}{V} + q\right)}{b \left(\frac{1}{V} + q\right) \left(1 + \frac{r' b_0}{r'' d'} q\right) - b_0 q}, \quad (9)$$

As a result instead of (1)-(5) we obtained equations

$$Aq^2 + Bq - Cq - \frac{W\delta}{V} = 0, \quad (10)$$

$$m = \frac{g_1}{2g_2} \left[ \sqrt{1 + \frac{4g_2}{g_1^2} W} - 1 \right], \quad (11)$$

where the following designations are introduced:

$$b_0 = \frac{\alpha' r' d'}{r' d'' + k'' (r' + r'')}, \quad \delta = \frac{r' (d'' + k'')}{r' d'' + k'' (r' + r'')}, \quad (12)$$

$$A = \gamma \frac{r' b_0}{r'' d'}, \quad B = W \frac{b_0}{d'} \left(1 - \frac{r'}{r''}\right) + \frac{amb_0}{b} \left(1 + \frac{r' k''}{r'' d'}\right) + \gamma \left(1 + \frac{r' b_0}{V d' r''} + \frac{k' r' b_0}{d' r'' b}\right),$$

$$C = \left(1 - \frac{b_0}{b}\right) (W\delta - kn_0) - \frac{Wb_0}{d' V} \left(1 - \frac{r'}{r''}\right) - \frac{\gamma}{V},$$

$$k = \frac{(d' + k') k' r'' + (d'' + k'') k' r'}{r' d'' + k'' (r' + r'')}, \quad n_0 = \frac{am + \gamma + b_0 \frac{W}{d'}}{b - b_0}.$$

Numerical estimation (see below) shows that the terms corresponding to account of spontaneous light radiation, proportional to  $1/V$ , in expressions B and C can always be discarded.

In the region of not too large  $q$ , including prethreshold, threshold and superthreshold laser operating modes, it is possible in (10) to discard the term with  $q^2$ . The quadratic equation for  $q$  being obtained as a result has the solution

$$q = \frac{1}{2B} \left[ C + \sqrt{C^2 + 4B \frac{W\delta}{V}} \right]. \quad (13)$$

Here  $4B \frac{W\delta}{V}$  is many orders smaller than  $C^2$  (see estimates below). Laying out the radical in (13), for  $q$  we obtain substantially different values in the prethreshold ( $C < 0$ ) and in superthreshold ( $C > 0$ ) regions:

$$q = -\frac{W\delta}{CV}. \quad (14)$$

$$q = \frac{C}{B}. \quad (15)$$

respectively.

It is easy to determine the threshold value of pumping  $W$ , with which sign  $C$  is changed and the laser regime is started. Let us write it out for two limiting cases:

1) With

$$\frac{4g_2}{g_1^2} W \ll 1 \quad (16)$$

according to (11)  $m = W/g_1$ . In this case the superthreshold regime occurs during pumpings

$$[W > \gamma \left[ \frac{b-b_0}{k} \delta - \frac{a}{g_1} - \frac{b_0}{d'} \right]^{-1}]. \quad (17)$$

it is necessary so that would be fulfilled condition

$$\frac{b-b_0}{k} \delta - \frac{a}{g_1} - \frac{b_0}{d'} > 0. \quad (18)$$

2) With

$$\frac{4g_2}{g_1^2} W \gg 1, \quad m = \sqrt{\frac{W}{g_2}}. \quad (19)$$

superthreshold regime is realized with pumpings

$$W > \left\{ \frac{\frac{a}{Vg_2} + \sqrt{\frac{a^2}{g_2^2} + 4\gamma \left[ \frac{\delta}{k} (b-b_0) - \frac{b_0}{d'} \right]}}{2 \left[ \frac{\delta}{k} (b-b_0) - \frac{b_0}{d'} \right]} \right\}^2 \quad (20)$$

with the fulfillment of condition

$$\frac{\delta}{k} (b-b_0) - \frac{b_0}{d'} > 0. \quad (21)$$

Let us examine now the region of large  $q$ , when in (10) it is necessary to retain the cubic term, but term  $W\delta/V$  can be disregarded. In this case

$$q = \frac{1}{2A} [-B + \sqrt{B^2 + 4AC}]. \quad (22)$$

This solution when  $4AC \ll B^2$  will coincide with (15). The quantum yield of the laser case of very large pumping powers ( $W \rightarrow \infty$ ). In this case  $B \rightarrow \beta W$ ,  $C \rightarrow \xi W$ , where coefficients  $\beta$  and  $\xi$  do not depend on  $W$  and can be obtained from (12).

With  $\beta > 0$

$$q \rightarrow \frac{\zeta}{\beta}, \quad \eta \rightarrow 0. \quad (24)$$

With  $\beta < 0$

$$q \rightarrow \frac{W|\beta|}{A}, \quad \eta \rightarrow \frac{\gamma_0|\beta|}{A}. \quad (25)$$

With  $\beta = 0$

$$q \rightarrow \sqrt{\frac{\zeta W}{A}}, \quad \eta \rightarrow 0. \quad (26)$$

In case (16)

$$\beta = \frac{b_0}{d'} \left(1 - \frac{r'}{r}\right) + \frac{ab_0}{g_1 b} \left(1 + \frac{r'k'}{r'd'}\right); \quad \zeta = \frac{b - b_0}{b} \delta - \frac{k}{b} \left(\frac{a}{g_1} + \frac{b_0}{d'}\right). \quad (27)$$

In case (19)

$$\beta = \frac{b_0}{d'} \left(1 - \frac{r'}{r}\right), \quad \zeta = \frac{b - b_0}{b} \delta - \frac{kb_0}{bg_1}. \quad (28)$$

The most urgent is case  $\beta < 0$ , since in this case is obtained the greatest quantum yield, namely

$$\eta \rightarrow \frac{\gamma_0}{\gamma} \begin{cases} 1 - \frac{r'}{r} - \frac{a}{g_1 b} \left(k' + \frac{r'd'}{r'}\right) & \text{при } g_2 = 0. \\ 1 - \frac{r'}{r} & \text{при } g_2 > 0. \end{cases} \quad (29)$$

Key: (a) when.

If  $b_0 = 0$ , for example, in the case of the absence of light absorption by quasi-molecules in the second electron state, then for  $q$  a simple expression is obtained at any superthreshold values of  $W$ :

$$q = \frac{1}{\gamma} \left[ W\delta - \frac{k}{b} (am + \gamma) \right]. \quad (30)$$

In this case  $\eta$  increases monotonically with  $W$  and in the limit of large  $W$

$$\eta \rightarrow \frac{\gamma_0}{\gamma} \begin{cases} \delta - \frac{ak}{bg_1} \stackrel{(a)}{\text{при}} g_2 = 0, \\ \delta \stackrel{(a)}{\text{при}} g_2 > 0. \end{cases} \quad (31)$$

Key: (a) when.

These values of  $\eta$  always exceed (29).

In the conclusion of this paragraph we make some estimates. Both in the impulse and the stationary regime the speed of the laser process is controlled by the speed of recombination  $r'n^2$ . For the laser of type [9] with thermal speed of molecules  $u=5 \cdot 10^4 \text{ cm} \cdot \text{s}^{-1}$ ,  $v=10^{-23} \text{ cm}^3$  and  $n=10^{17} \text{ cm}^{-3}$  this speed is on the order of  $2.5 \cdot 10^{22} \text{ cm}^{-3} \cdot \text{s}^{-1}$ . With  $\eta=1$  and energy of radiated quantum 2 eV this corresponds to the power of light release in a unit of volume  $8 \cdot 10^4 \text{ W} \cdot \text{cm}^{-3}$ . In the stationary regime, as was mentioned above,  $r'n^2$  is the upper limit of pumping power  $W$ .

In kinetic equations (1)-(5) terms  $g_{,m}$  and  $g_{,m}^2$  are linear and quadratic, in terms of concentration, speeds of removal of reaction products. Linear law is realized, for example, with pumping of products out of the working volume or during their removal by open flow of gas, during destruction of products with the aid of their chemical reaction with a third gas, during spontaneous

phototransitions and thermal transitions of electrons in reaction products, if the latter are excited, etc. With removal of products by an open flow of gas  $g_1 = U/l$ , where  $U$  - speed of gas flow, and  $l$  - size of working volume of gas in the direction of flow. Let us take for estimates  $U = 10^3 \text{ cm} \cdot \text{s}^{-1}$ ,  $l = 1 \text{ cm}$ , then  $g_1 = 10^3 \text{ s}^{-1}$ . Approximately the same or somewhat larger value of  $g_1$  can be achieved during removal of products with the aid of chemical reaction [4].

Quadratic law of removal of products is realized when they react during collision with each other. If this reaction occurs with participation of a molecule of a third gas, the concentration of which is  $10^{22} \text{ cm}^{-3}$ , then  $g_2 \sim 5 \cdot 10^{-13} \text{ cm}^3 \cdot \text{s}^{-1}$ .

For check of criteria (16) and (19) we note that  $\frac{4g_2}{g_1^2} W = 1$  with  $W = 5 \cdot 10^{22} \text{ cm}^{-3} \cdot \text{s}^{-1}$ .

The speeds of thermal dissociation of quasi-molecules  $d'$  and  $d''$  in case a) are on the order of inverse time of gas-kinetic contact of two molecules, and in case b) - one-two orders less. Let us take  $d' \sim d'' \sim 10^{11} - 10^{12} \text{ s}^{-1}$ .

Let us estimate the speed of the thermal chemical reaction  $k'$ , assuming that in the quasi-molecule is accomplished the elementary act of the reaction almost with each of its gas-kinetic collision. As

a result is obtained  $k \sim k' \sim 2.5 \cdot 10^4 \text{ s}^{-1}$ .

$b/V$  is the probability of spontaneous radiation of a molecule into the working mode in a unit of time. For the probability of spontaneous radiation in a unit of time in all modes of the spectrum of luminescence we take value  $10^4 \text{ s}^{-1}$ , the number of modes in the region of the spectrum of luminescence we assume equal to  $10^{12} \text{ V cm}^{-3}$  [9]. Then  $b \sim 10^{-8} \text{ cm}^3 \cdot \text{s}^{-1}$ . It is possible to show that where  $\epsilon$  - rotational-vibrational energy of a molecule of product immediately after phototransition. Accepting  $\epsilon = 0.5 \text{ eV}$ ,  $\epsilon/T = 20$ , we obtain  $a/b \sim 10^{-4} - 10^{-5}$ .

During estimates we disregard the absorption of light by quasi-molecules in the second electron state, assuming  $a'' = b_0 = 0$ ,  $\gamma_0 = cD/L$ , where  $D$  - transmission coefficient of mirrors,  $L$  - distance between them. Assuming  $D = 0.03$  and  $L = 30 \text{ cm}$ , we obtain  $\gamma_0 \sim 3 \cdot 10^7 \text{ s}^{-1}$ ,  $\gamma$  slightly exceeds this value. Disregarding  $k''$  in comparison with  $d''$ , we obtain  $\delta = 1$ .

With the above-presented values of parameters inequality (18) is reduced to inequality  $g_1 > k a/b = 0.25 - 2.5 \text{ s}^{-1}$ , which is knowingly fulfilled. Condition (7) acquires the form  $W > \gamma k / b \delta = 7.5 \cdot 10^{21} \text{ cm}^{-3} \cdot \text{s}^{-1}$ . Thus, threshold pumping power lies in the region determined by (16), which justifies the use of formulas (17), (18).

In the expression for quantum yield (31) it is possible to disregard term  $ak/bg_1$ . As a result  $\eta \rightarrow \gamma_0/\gamma$ , i.e., losses in quantum yield are caused exclusively by absorption of light in the mirrors.

#### Reaction of exchange or substitution.

In this paragraph will be examined the reactions, the products of which are two unconnected molecules. Such are, for example, substitution reaction  $AB+C=AC+B$  or exchange reaction  $AB+CD=AC+BD$ . For simplicity we will be limited to cases when the collided initial particles form quasi-molecules only in one single electron state. Let us designate the concentration of such quasi-molecules  $n'$ . As a result of induced phototransition or thermal transition of electrons in such quasi-molecule, it is transformed into an unstable quasi-molecule of reaction product. Concentration of the latter -  $m'$ . These quasi-molecules are each decomposed into two molecules, which also are the final products of reaction. Their concentration -  $m$ . For example, during substitution reaction the concentration of initial molecules  $AB$ , and also  $C$  -  $n$ , concentration of quasi-molecules  $ABC$  in initial electron state -  $n'$ , concentration of quasi-molecules  $ABC$  in final electron state (with lower energy) -  $m'$ , concentration of molecules  $AC$ , and also  $B$  -  $m$ .

Kinetic equations have such a form:

$$\frac{dn}{dt} = W - r'n^2 + d'n' = 0, \quad (32)$$

$$\frac{dn'}{dt} = r'n^2 - d'n' - k'n' - b\left(\frac{1}{V} + q\right)n' + aqm' = 0, \quad (33)$$

$$\frac{dm'}{dt} = r'm^2 - d'm' + k'n' + b\left(\frac{1}{V} + q\right)n' - aqm' = 0, \quad (34)$$

$$\frac{dm}{dt} = -r'm^2 + d'm' - g_1m - g_2m^2 = 0, \quad (35)$$

$$\frac{dq}{dt} = b\left(\frac{1}{V} + q\right)n' - aqm' - \gamma q = 0. \quad (36)$$

The majority of terms in these equations have the same meaning as in the previous paragraph. The difference of the examined case from the previous involves the fact that the absorption of light of the working mode by quantum, represented by term  $aqm'$ , is accomplished by unstable quasi-molecules in the final electron state, the concentration of which  $m'$  is small.

From equations (32)-(36) is also obtained formula (11) with limiting cases (16) and (19). Further, from (32)-(36) follows

$$n^2 = \frac{1}{r'} \left[ W \left( 1 + \frac{d'}{kr'} \right) - \frac{d'\gamma}{k'} q \right]. \quad (37)$$

$$n' = \frac{1}{k'} (W - \gamma q), \quad (38)$$

$$m' = \frac{1}{g_2} (W + r'm^2). \quad (39)$$

For  $q$  are obtained formulas (13)-(15) (as before  $4BW/V \ll C^2$ ), but the

expressions for coefficients are simpler:

$$B = \gamma, \delta = 1, C = \xi W + \frac{k' a r' g_1^2}{2 b d' g_2^2} \sqrt{1 + \frac{4 g_2 W}{g_1^2}} - \frac{k' \gamma}{b} - \frac{\gamma}{V}, \quad (40)$$

$$\xi = 1 - \frac{a k'}{b d'} \left(1 + \frac{r'}{g_2}\right).$$

The laser regime takes place in case (15), when  $q$  is many orders greater than in case (14). According to (40), with  $\xi > 0$   $C$  monotonically increases with  $W$ , changing from negative to positive values. Change of the sign of  $C$  occurs in the region determined by (19). The corresponding threshold value of  $W$  is determined by inequality

$$W > \frac{k' \gamma}{\xi b}. \quad (41)$$

In this case, with large  $W$ , quantum yield

$$\eta \rightarrow \frac{\gamma_0}{\gamma} \xi. \quad (42)$$

With  $\xi < 0$  with growth of  $W$ ,  $C$  passes through maximum and then diminishes to  $-\infty$ . If in the maximum  $C > 0$ , then a region of values  $W$  exists, limited on two sides, in which the laser regime is realized (15). Condition  $\xi < 0$  is not compatible with (19). In limiting case (16) the boundaries of the region of laser regime are determined by formulas

$$W_1 < W < W_2, \quad W_{1,2} = \frac{g_2^2 b d'}{2 a k' r'} \left[ 1 - \frac{a k'}{b d'} \pm \sqrt{\left(1 - \frac{a k'}{b d'}\right)^2 - \frac{4 k'^2 a r' \gamma}{b^2 d' g_1^2}} \right]. \quad (43)$$

It is necessary that the maximum value of C be positive:

$$C_{\max} = \frac{g_1^2 b d^2}{4 a k' r^2} \left( 1 - \frac{a k'}{b d^2} \right)^2 - \frac{k' \gamma}{b} > 0. \quad (44)$$

With  $\xi=0$  threshold condition has the form

$$W > \frac{\gamma^2 g_2^2 d^2}{a^2 r^2 g_1^2} \left[ 1 - \left( \frac{a r^2 g_1^2}{2 \gamma d^2 g_2^2} \right)^2 \right], \quad (45)$$

and  $\eta \rightarrow 0$  with  $W \rightarrow \infty$ .

#### Conclusion.

Equations (1)-(5) and (32)-(36) investigated above describe not only the kinetics of a chemical laser, but simultaneously the kinetics of a chemical reaction self-induced by light, occurring in the resonator. The chemical reaction is accomplished in parallel by two ways: ordinary thermal means and with induced radiation of light. With pumping power W below the threshold value the first mechanism dominates, with W above the threshold value - the second mechanism. Material in the article is stated as applied to lasers. However, all the results are easy to reformulate and are applicable to kinetics of chemical reaction.

In the chemical laser both in stationary and in impulse regimes

the speed of the entire laser process is controlled by the rate of bimolecular recombination of initial molecules  $r'n^2$ . In an ordinary chemical laser the act of such recombination is the elementary act of the chemical reaction. In the laser of type [9] the speed of the mentioned recombination - number of simple gas-kinetic collisions in a unit of volume per second, which considerably exceeds the speed of the bimolecular in an ordinary chemical laser. Correspondingly the maximum power of light release in the laser of type [9] can be greater.

In the case of addition reaction, if  $b_0 \neq 0$ , according to (24)-(26) with  $\beta > 0$  the concentration of photons in the resonator  $q$  with growth of  $W$  approaches constant value, and  $\eta \rightarrow 0$ . With  $\beta < 0$   $q$  is increased in proportion to  $W$ , and quantum yield approaches constant value. With  $\beta = 0$   $q$  is changed in proportion to  $\sqrt{W}$ , and  $\eta \rightarrow 0$ . Therefore case  $\beta < 0$  is of the greatest interest. In this case, according to (29), the greatest quantum yield is obtained with  $g_2 > 0$ , i.e., when the speed of removal of reaction products is proportional to the square of their concentrations.

However, the most favorable is case  $b_0 = 0$  (there is no absorption of generated light by quasi-molecules in the second electron state). Then, according to (31), the greatest quantum yield is obtained also with  $g_2 > 0$ . In this case it is important to emphasize that the thermal

chemical reaction competing with induced phototransition, being characterized by coefficient  $k'$ , does not reduce the quantum yield in the limit of large  $W$ , since in this case the speed of the reaction induced by light increases so much that the heat reaction parallel to it turns out to be not substantial. On the contrary, the chemical reaction, during which are formed quasi-molecules in the second electron state and which is characterized by the product of  $r'' \cdot k''$ , lowers the quantum yield, since even in limit  $W$ ,  $q \rightarrow \infty$  the speed of the reaction, during which are formed quasi-molecules in the first electron state, does not become infinite, and is limited by value  $r'n^2$ .

In the case of exchange or substitution reaction, according to (40), (42), with  $\xi > 0$  the concentration  $q$  increases in proportion to  $W$ , and the quantum yield approaches constant value. Case  $\xi > 0$  is realized with rather large  $g_1$ . With  $\xi > 0$  the laser regime is realized in the region of values of  $W$ , limited on both sides (see (43)), with the fulfillment of necessary condition (44). This region is expanded with the growth of  $g_1$ . With  $\xi = 0$   $q$  increases in proportion to  $\sqrt{W}$ , and quantum yield approaches zero. The most favorable is the case of positive and close to one  $\xi$ . It is necessary to emphasize that during the exchange or substitution reaction the approaching initial molecules cannot form quasi-molecules in the final electron state, in contrast to the addition reaction. Therefore during the exchange

reaction values  $n''$ ,  $a''$  and  $k''$  do not figure in kinetic equations.

The estimates show that threshold values of pumping  $W$  can be achieved, for example, a) by delivery of initial molecules and by removal of reaction products by open flow, b) by obtaining of initial molecules as products of another preceding chemical reaction; c) by obtaining of initial molecules as a result of decomposition of stable molecules by light, discharge in gas, beam of fast particles etc.

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## THE HEAT PUMPING OF PHOTOINDUCED CHEMICAL REACTION

V. A. Kochelap

Recently Pekar indicated the possibility of stimulating the chemical reaction with light [1]. For accomplishment of the photoinduced chemical reaction (FKhR) it is necessary to create a rather large concentration of chemically active molecules in the reactor [1, 2]. In this report on an example of the reaction of recombination of atoms  $A+B=AB$  we will show that for obtaining the necessary concentration of active molecules (atoms) it is possible to use known thermal methods (rapid heating or cooling) [3-5].

Let us examine equilibrium partially dissociated gas, initially located at temperature  $T_0$ . With cooling of such gas during time  $t_{cool} \lesssim \tau_{rec}$ , where  $\tau_{rec}$  - characteristic time of the recombination reaction, equilibrium is disturbed, and the chemical process will occur by means of recombination. If, moreover, is provided rapid relaxation of excited vibrational states of molecule AB (with characteristic time  $\tau_{rel}$ ), then the existence of FKhR becomes possible

[1, 2]. The conditions, necessary for realization of FKHR, can be presented in the form

$$\tau_{\text{rec}} \geq \tau_{\text{coll}}, \quad \tau_{\text{rec}} \gg \tau_{\text{rel}} \quad (1)$$

Times  $\tau_{\text{rec}}$  and  $\tau_{\text{rel}}$  can be written approximately in the following manner:  $\tau_{\text{rec}}^{-1} = z_{\text{rec}} \omega u^{3/2} n^2$  and  $\tau_{\text{rel}}^{-1} = z_{\text{rel}} \omega u^{2/2} n$ , where  $z_{\text{rec}}$  and  $z_{\text{rel}}$  - effectiveness of collisions, leading to the act of recombination and relaxation respectively,  $u$  - average thermal velocity of particles in gas,  $v$  - volume, occupied by one atom,  $n$  - concentration of particles in gas. Accepting that  $z_{\text{rel}} = 0.1$ ,  $z_{\text{rec}} = 0.001$ ,  $u = 10^5$  cm/s,  $v = 10^{-23}$  cm<sup>3</sup>,  $n = 10^{22}$  cm<sup>-3</sup>, we obtain  $\tau_{\text{rec}} = 3 \cdot 10^{-6}$  s,  $\tau_{\text{rel}} = 3 \cdot 10^{-6}$  s. Since, according to [5], it is possible to provide  $\tau_{\text{coll}} = 10^{-4} - 10^{-5}$  s, then conditions (1) can be satisfied.

The amplification factor of the light wave by partially dissociated gas  $\alpha$  can be presented in the form [2]

$$\alpha = \frac{(2\pi)^{3/2} e^2 |u_{g'g}(r_j)|^2 \omega_0 \mu^{1/2} r_j^2}{c \omega T_k^{1/2} |F_g(r_j) - F_{g'}(r_j)|} \left| \frac{(2\pi)^{3/2} r_0^2 T_k^{1/2} p_g(r_j)}{\omega_0 \mu^{1/2}} n_A n_B - n_{AB} e^{\frac{U_g(r_0) - U_{g'}(r_j)}{T_k}} \right| \quad (2)$$

In (2) it is accepted that phototransition occurs between electron terms  $U_g(r)$  and  $U_{g'}(r)$  ( $U_g(r) > U_{g'}(r)$ ) at frequency  $\omega$ ;  $r_j$  - value of internucleus distance  $r$ , satisfying equality  $U_g(r_j) - U_{g'}(r_j) = \hbar \omega$ .

$F_g(r) = -\partial U_g / \partial r$ ;  $\omega_0$ ,  $r_0$  - vibration frequency and equilibrium distance between nuclei in state  $g'$ ;  $u_{g'g}(r)$  - matrix element of operator of electron velocity,  $p_g(r_j)$  is determined by expression

$$\rho_g(r) = \frac{1}{G} \begin{cases} e^{-\frac{U_g(r)}{T_k}}, & U_g(r) > 0, \\ 2 \sqrt{\frac{-U_g(r)}{\pi T_k}} + e^{-\frac{U_g(r)}{T_k}} \left[ 1 - \Phi \left( \sqrt{\frac{-U_g(r)}{T_k}} \right) \right], & U_g(r) < 0. \end{cases} \quad (3)$$

where  $G$  - number of states, coinciding with  $r \rightarrow \infty$ ,  $\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x dt e^{-t^2}$ .

$T_k$  - final temperature, to which the gas is cooled.

Expressions (2) and (3) are introduced into the assumption that  $T_n, T_k \gg h\omega$ .

If inequality (1) is fulfilled, then it is possible to assume

$$n_A n_B = \frac{\mu^{1/2} \omega_0 n_{AB}}{(2\pi)^{3/2} r_0^2 T_n^{1/2}} e^{-\frac{D}{T_n}}, \quad (4)$$

$D$  - energy of dissociation of molecule AB,  $D \gg T_n$ .

Amplification factor of light wave  $\alpha > 0$  will take the form:

$$\rho_g(r_j) \sqrt{\frac{T_k}{T_n}} e^{-\frac{D}{T_n}} > e^{\frac{U_g(r_0) - U_g(r_j)}{T_k}}. \quad (5)$$

From formula (5) we see that during phototransitions at such frequencies, to which corresponds  $r_j \neq r_0$ , sufficiently thorough cooling can lead to  $\alpha > 0$ . In such a case when  $T_k$  is so small that inequality (5) is intensified, in (2) it is possible to disregard

absorption by AB molecules, and the condition of appearance of FKHR will take the form

$$n_{AB} > \frac{1 - \kappa \omega \nu_0^2 T_n^{-1/2} |F_g(r_1) - F_g(r_2)| e^{D/T_n}}{L (2\pi)^{3/2} e^2 |v_{ggs}(r_1)|^2 r_1^2 \omega_0 \mu^{1/2} p_g(r_1)} \quad (6)$$

here  $\kappa$  - reflection coefficient of mirrors,  $L$  - length of reactor.

As an example let us consider the recombination reaction of atoms Br (radiation appearing with this reaction was observed in work [6]). In work [7] it is shown that this radiation corresponds to phototransition between states  ${}^2\Pi_u$  and  ${}^2\Sigma_g^+$  of molecule  $Br_2$ . For molecule  $Br_2$  it is possible to assume  $\omega_0 = 10^{13} \text{ s}^{-1}$ ,  $r_0 = 2.28 \text{ \AA}$ ,  $D = 2.88 \cdot 10^{-13} \text{ erg}$ . Accepting  $\omega = 10^{15} \text{ s}^{-1}$ , we obtain  $r_1 = 2.6 \text{ \AA}$ ,  $|F_g(r_1) - F_g(r_2)| = 2.5 \cdot 10^{-4} \text{ erg/cm}$ ,  $|v_{ggs}(r_1)| = 10^7 \text{ cm/s}$ ,  $U_g(r_1) - U_g(r_0) = 1.4 \cdot 10^{-13} \text{ erg}$ ,  $p_g(r_1) \approx 0.5$ . The substitution of these values in expression (5) shows that amplification will take place at  $T_n \geq 2T_k$ . If we assume  $T_n = 2000^\circ \text{ K}$ , then from (6) it follows that FKHR will be realized at  $T_k \leq 1000^\circ \text{ K}$  and  $n_{Br_2} \geq 5.6 \cdot 10^{18} \text{ cm}^{-3}$ .

According to [6], recombination goes mainly by radiation means:  $Br + Br \rightarrow Br_2 + h\nu$ , so that it is possible to accept [1] that  $\tau_{pek} \approx \alpha \omega^2 \Delta\omega / \pi^2 c^2 n$ . Here  $\alpha$  is determined by formula (2) with  $n_{AB} = 0$ ,  $\Delta\omega$  - width of line of luminescence. With  $\Delta\omega = 0.3 \omega$  and accepted values of parameters  $\tau_{pek} = 3 \cdot 10^{-3} \text{ s}$ . Such numerical value of  $\tau_{pek}$  makes it

possible to fully satisfy the first of inequalities (1) in such volumes of gas, in which the length of the path of the light beam is located in accordance with the estimate  $L=10$  cm accepted above. Actually, from work [5] it follows that cooling of layer Br, 10 cm thick from 2000 to 1000° K can be accomplished in a chemical shock tube during time  $\tau_{\text{cool}} = 4 \cdot 10^{-4}$  s. The use of rapidly expanding (at supersonic speed) gas flow [4, 5] makes it possible to reduce to values  $10^{-4}-10^{-5}$  s, where realization of  $L=10$  cm is also fully possible (see recent work [8]). Finally, for estimate of the second of inequalities (1) let us note that according to [9] for Br, with  $T=1000^\circ$  K is realized value  $\tau_{\text{rel}} = 0.5 \cdot 10^{-4}$  s.

Let us note that because of the large density of states of continuous spectra the gas becomes substantially dissociated already at temperatures 1500-2000° K (see formula (5)). This circumstance makes it possible to accomplish FKhr and radiation on electron phototransitions with not too high initial temperatures (compare with [3-5]).

Fully analogously it is possible to show that by thermal methods (rapid heating or cooling) it is possible to accomplish other types of FKhr (such as reactions of exchange, substitution etc.).

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