

Influence of oxygen on the energy characteristics of a chemical pulsed hydrogen fluoride laser

V.I. Igoshin, A.I. Klyukach, S.Yu. Pichugin

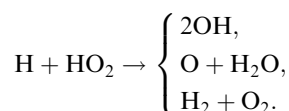
Abstract. The specific energy yield is calculated as a function of the pressure of oxygen and SF₆ buffer gas taking into account the secondary processes with the participation of the HO₂ radical. The results of these calculations are compared with the experimental data. A significant role of reactions with the participation of the HO₂ radical is revealed. A numerical analysis of the experiments also makes it possible to appreciably refine the rate constant of a process of interrupting a chain reaction with the participation of H₂ and F₂ as third bodies.

Keywords: pulsed chemical laser, kinetic model, chain breakage, specific laser output energy.

1. Introduction

A specific feature of chemical lasers based on a chain reaction between fluorine and oxygen is an instability of the H₂ + F₂ mixture that leads to an explosive behaviour of the reaction even before its initiation. To suppress a spontaneous ignition of the mixture, it is doped with oxygen that decelerates the development of its explosion (spontaneous ignition) predominantly due to the breakage of the H + O₂ + M → HO₂ + M chain. The chain breakage rate must be sufficiently high for the energy branching of the H₂* + F₂ → H + HF + F chain to be suppressed. This is achieved at a sufficiently high relative content of O₂ and a total mixture pressure exceeding the second limit of ignition [1].

However, as was shown experimentally, the laser output energy rapidly decreases with increasing the O₂ concentration. The mechanism of influence of oxygen on the energy characteristics of an H₂ – F₂ laser has not as yet been explained quantitatively. From the complete kinetic scheme of the processes in the H₂ + F₂ + O₂ + He system [1], it follows that the presence of oxygen in the working mixtures may lead to an increased relaxation rate of the excited HF molecules due to the secondary processes with the participation of the HO₂ radical [1]:



H₂O molecules and OH radicals produced in these reactions are efficient catalysts of the HF* vibrational relaxation. The secondary processes were ignored in earlier computational and theoretical studies. The objective of this work is to clarify their role in the laser energy characteristics. Here, the specific output energy is calculated as a function of the pressure of oxygen and the SF₆ buffer gas taking into account the secondary processes.

2. Kinetic laser model

A multilevel model of an H₂ – F₂ laser [2] supplemented with the aforementioned secondary processes with the participation of the HO₂ radical was used in our calculations. The HF* relaxation rate for the interaction with OH is taken equal to that for the HF self-relaxation, which is determined by the closeness of the physical parameters of the interaction for molecular collisions. When calculating numerically the characteristics of a multilevel H₂ – F₂ laser, we solved the equations for the populations n_v of the vibrational levels of HF molecules ($v = 0, 1, \dots, 7$), chemical-kinetics equations in the H₂ – F₂ laser medium [1], and equations for the average store of H₂ vibrational quanta and the temperature of the gas medium.

In the equations for n_v , the VV exchange between the levels of HF molecules ($v = 0, 1, \dots, 7$) and the VV' exchange between HF and H₂ molecules were taken into account. A harmonic-oscillator approximation was used for the VV' exchange. It was assumed in the calculations that the characteristic time of the rotational relaxation is $\tau_0 = (\pi\Delta\nu_L)^{-1}$, where $\Delta\nu_L$ is the homogeneous half-width of the Lorentzian profile of the HF line [3], $\Delta\nu_L = \sum \gamma_M p_M$ (p_M is the partial pressure of the M component), $\gamma_{\text{H}_2} = \gamma_{\text{O}_2} = 0.02 \text{ cm}^{-1} \text{ atm}^{-1}$, $\gamma_{\text{F}_2} = 0.035 \text{ cm}^{-1} \text{ atm}^{-1}$, $\gamma_{\text{HF}} = 0.09 \text{ cm}^{-1} \text{ atm}^{-1}$, and $\gamma_{\text{He}} = 0.0055 \text{ cm}^{-1} \text{ atm}^{-1}$. The parameter γ_{SF_6} in our calculations was assumed equal to $0.9 \text{ cm}^{-1} \text{ atm}^{-1}$ [4, 5].

3. Analysed experiments

The first of the experiments was performed on a setup using the third harmonic of a Nd laser [5]. The specific energy yield of an H₂ – F₂ laser was studied as a function of the SF₆ pressure in a mixture of F₂ : H₂ : O₂ : He : SF₆ = 75 : 25 : 7.5 : 50 : (50 – 600) Torr. The initial concentration

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Table 1. Rate constants of the $\text{H} + \text{O}_2 + \text{H}_2 = \text{HO}_2 + \text{H}_2$ reaction [21] ($k = k_{\text{H}_2}$) and methods for determining them.

Constant number	T/K	$\lg k$	$\lg A$	n	$E/\text{kcal mol}^{-1}$	Method	References
1	293	13.84	–	–	–	I	[7]
2	293	14.52	–	–	–	II	[8]
3	293	14.64	–	–	–	III, IV	[9]
4	293	16.60	–	–	–	III	[10]
5	293	17.46	–	–	–	Estimate	[11]
6	293	17.26	–	–	–	–	[12]
7	293–319	17.80	–	–	–	II	[13]
8	293, 793	–	15.2	0	–3.5	–	[14, 15]
9	293–803	–	15.7	0	-1.3 ± 0.5	V	[16]
10	300–647	–	–	–	–4.8	I	[17]
11	700–800	–	15.06	0	–3.55	VI	[18]
12	770	15.73	–	–	–	VII	[19]
13	793	~ 16.16	–	–	–	VII	[20]
14	293–813	–	15.50 ± 0.10	0	-1.89 ± 0.21	–	–
15	293–813	–	22.03 ± 0.47	-2.08 ± 0.17	0	–	–
16	–	–	18.32	–1	–	–	[4]

Note. Rate constants are represented as $k = AT^n \exp[-E/(RT)]$; the dimension of k is $\text{cm}^6 \text{mol}^{-2} \text{s}^{-1}$; the temperature dependences of the constants 1–7, 12, 13, and 16 were assumed proportional to T^{-1} . The notation of methods is as follows: (I) producing active particles by a photochemical method using mercury as a sensitizer; (II) photochemical reaction; (III) producing active particles in an electric discharge; (IV) jet technique of conduction the reaction; (V) using a computer; (VI) by the ignition threshold; and (VII) reaction occurs in a flame.

of free atoms measured in these experiments was $N_a(0) = 1.5 \times 10^{17} \text{cm}^{-3}$.

In the second experiment, we measured the specific energy yield as a function of the oxygen pressure in a working mixture of $\text{F}_2 : \text{H}_2 : \text{He} : \text{O}_2 = 300 : 100 : 100 : 3$ (or 6, 15, 30) Torr. The reaction was initiated by an electron beam with a large rectangular cross section that propagated in the direction perpendicular to the laser optical axis [6]. The electron beam was formed by an accelerator with an initiation duration of 1 μs . This accelerator provides a concentration of active centres in the working medium of the chemical laser comparable to that reached upon a high-power optical initiation. The absolute concentration of the accelerator-produced F atoms was determined by comparing the calculated and measured specific output energies using a variation of the initiation rate constant at a single (the lowest) O_2 concentration value.

4. Calculation results

The specific laser-energy yield was calculated for these two experiments. For SF_6 -containing mixtures, the $\text{H} + \text{O}_2 + \text{SF}_6 \rightarrow \text{HO}_2 + \text{SF}_6$ reaction plays the main role in the chain breakage. For mixtures without SF_6 , the chain breakage is determined to a significant degree by the participation of H_2 and F_2 as third bodies. Large discrepancies in the rate constants of the $\text{H} + \text{O}_2 + \text{H}_2 \rightarrow \text{HO}_2 + \text{H}_2$ reaction are pointed out in the literature (Table 1). Therefore, comparing the calculated and experimental pressure dependences of the specific output energy helps to appreciably refine the rate constant of the process of breaking the chain in which H_2 and F_2 participate as third bodies. The calculated and experimental dependences of the specific energy yield for the two experiments are shown in Figs 1 and 2. As is seen, the group of constants 5, 6, and 11 from Table 1 reproduces the experimental data with both the optical and electron-beam initiation to the highest accuracy (10%–15%). The other tabulated data on the chain breakage are obviously

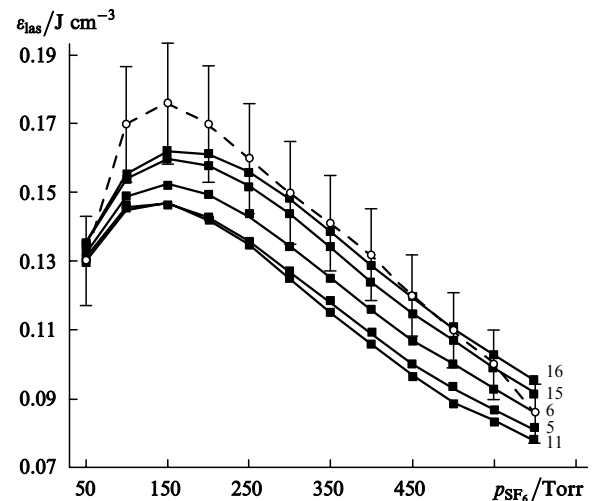


Figure 1. Experimental (○) and calculated (■) dependences of the specific output energy of an $\text{H}_2 - \text{F}_2$ laser, which is initiated by the third harmonic of a Nd laser, on the SF_6 pressure at various rate constants of the $\text{H} + \text{O}_2 + \text{H}_2 \rightarrow \text{HO}_2 + \text{H}_2$ reaction (T is measured in Kelvins): $k = 10^{17.46} (300/T)$ (5), $10^{17.26} (300/T)$ (6), $10^{15.06} \exp(1790/T)$ (11), $10^{22.03} T^{-2.08}$ (15), $7 \times 10^{15} (300/T)$ (16). The experimental accuracy is taken equal to 10% (shown by vertical lines); the rate constant of the $\text{H} + \text{O}_2 + \text{F}_2 \rightarrow \text{HO}_2 + \text{F}_2$ reaction is taken equal to $k_{\text{F}_2} = 0.8k_{\text{H}_2}$ in accordance with [1]; the figures near the curves correspond to the numbering of the rate constants in Table 1.

inconsistent with the experiment with the electron-beam initiation. Note that, if the secondary processes are neglected, the agreement between the calculated and experimental dependences of the specific energy yield on the partial SF_6 pressure is much worse (Fig. 3).

5. Conclusions

The specific output energy of a pulsed HF chain-reaction laser calculated as a function of the O_2 and SF_6

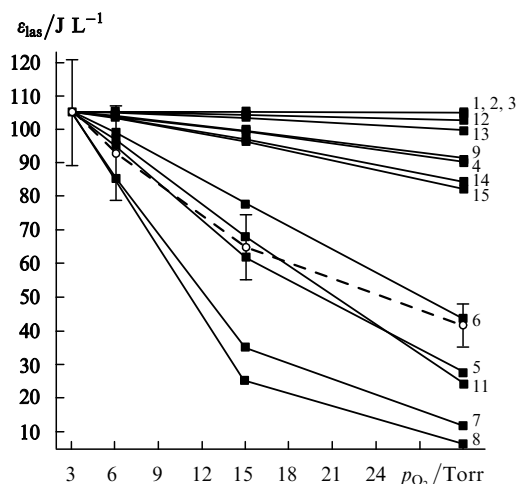


Figure 2. Experimental (○) and calculated (■) dependences of the specific output energy of an $\text{H}_2 - \text{F}_2$ laser, which is initiated by an electron beam, on the SF_6 pressure at various rate constants of the $\text{H} + \text{O}_2 + \text{H}_2 \rightarrow \text{HO}_2 + \text{H}_2$ reaction (T is measured in Kelvins): $k = 10^{13.84}(300/T)$ (1), $10^{14.52}(300/T)$ (2), $10^{14.64}(300/T)$ (3), $10^{16.6}(300/T)$ (4), $10^{17.46}(300/T)$ (5), $10^{17.26}(300/T)$ (6), $10^{17.80}(300/T)$ (7), $10^{15.5} \times \exp(1764.7/T)$ (8), $10^{15.7} \exp(655.5/T)$ (9), $10^{15.06} \exp(1790/T)$ (11), $10^{15.73}(300/T)$ (12), $10^{16.16}(300/T)$ (13), $10^{15.5} \exp(953/T)$ (14), $10^{22.03} \times T^{-2.08}$ (15). The experimental accuracy is taken equal to 15% (shown by vertical lines); the rate constant of the $\text{H} + \text{O}_2 + \text{F}_2 \rightarrow \text{HO}_2 + \text{F}_2$ reaction is taken equal to $k_{\text{F}_2} = 0.8k_{\text{H}_2}$ in accordance with Ref. [1]; the figures near the curves correspond to the numbering of the rate constants in Table 1 (the experimental data presented by S.D. Velikanov and V.D. Urlin were obtained on the facility described in Ref. [6]).

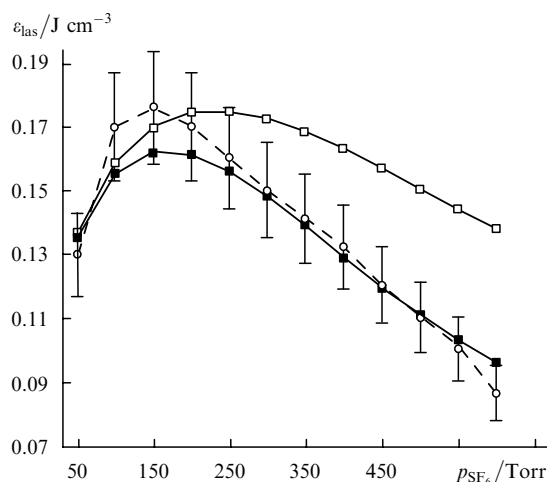


Figure 3. Experimental (○) and calculated dependences, that take into account (■) and neglect (□) the secondary processes, of the specific output energy of an $\text{H}_2 - \text{F}_2$ laser, which is initiated by the third harmonic of a Nd laser, on the SF_6 pressure. The experimental error is 10% (shown by vertical lines).

concentrations revealed a significant role of the secondary processes involving HO_2 radicals and made it possible to refine the rate constants of breaking the chain with H_2 and F_2 , which participate in it as third bodies, and to interpret quantitatively the dependence of the specific output energy on the partial O_2 concentration.

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