

Rotational disequilibrium and energetics of a chemical laser based on the chain reaction $H_2 + F_2$

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The effect of C_5F_{12} molecules on the energy characteristics of a pulsed chemical laser based on the $H_2 + F_2$ chain reaction is investigated experimentally. It is shown that the observed increase in the lasing energy following the addition of C_5F_{12} is accompanied by a slowing down of the chemical reaction. This experimental fact is attributed to an increase in the rate of the rotational relaxation of the HF molecules

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INTRODUCTION

Calculations were recently performed on the effect of the nonequilibrium distribution of HF molecules with respect to the rotational levels on the lasing of cw^[1] and pulsed^[2,3] chemical laser operating on the $H_2 + F_2$ reaction (henceforth designated $(H_2, F_2)CL$ for brevity). An earlier analysis^[3] of two extremal operating regimes of a laser with "instantaneous" and "frozen" rotational (R) relaxation has shown that the limiting value of the specific energy output of a laser with instantaneous R relaxation is 2-3 times larger than in the case of frozen relaxation. In addition, whereas in the case of instantaneous R relaxation the $V-V$ exchange processes between the HF molecules do not influence the energetics of the lasing,^[3-5] and the lasing is stopped as a result of $V-T$ relaxation of the HF molecules with one another, in the case of frozen R distribution the $V-V$ exchange leads in practice to vanishing of the inversion.^[3] Since the rate of the $V-V$ exchange is larger by approximately one order of magnitude by the rate of the $V-T$ relaxation,^[6,7] the R -equilibrium conditions are advantageous from the point of view of the depth of relaxation up to which the lasing can continue.

Experiments have shown that the corresponding rate constants of R relaxation of HF molecules^[6,9] on the main component of the $(H_2, F_2)CL$ mixture are small, and a noticeable transformation of the initial strong-disequilibrium R distribution^[10-12] takes place only after a large number of molecular collisions. The performed qualitative analysis^[3] attests to the fact that most realized $(H_2, F_2)CL$, especially if the initiation is strong enough, operate under conditions far from R equilibrium. On the other hand, in lasers operating on single-act non-chain processes, the conditions for fast R relaxation of the HF molecules were realizable either by strongly diluting the mixture with the inert gases He, Ar, and N_2 , or by introducing "good" R -relaxants, such as SF_6 and C_2F_6 .^[13,14] The attained kinetic lasing regime was such that the individual vibrational-rotational lines appeared in the strict sequence^[13] characteristic of R -equilibrium conditions. In addition, an increase was noted in the lasing intensity.^[14]

To our knowledge, no experimental investigations were made of the influence of R relaxation on the operation of $(H_2, F_2)CL$. These chemical lasers are unique in

that their parameters depend strongly on the kinetic regime of the chemical reaction,^[15-19] and this regime is determined in turn by factors connected with the thermal acceleration of the chemical process.^[5,20] As a result, investigations aimed at revealing the role of the R -relaxation processes in the lasing energetics are possible only if the rate of the chemical reaction is simultaneously controlled.

In the present study we have investigated the influence of the addition of C_5F_{12} molecules on the energetics of $(H_2, F_2)CL$. Owing to the large number of the vibrational degrees of freedom with frequencies close to the frequencies of the rotational transitions in the HF molecules, and to the absence at the same time of frequencies close to the frequency of the HF vibrational quantum, it seemed that the C_5F_{12} molecules should be good R relaxant and should at the same time not accelerate the vibrational relaxation of the HF molecules. The kinetics of the chemical reaction was monitored in the experiments by the method of kinetic spectroscopy against the consumption of the F_2 molecules.

EXPERIMENTAL PROCEDURE

The experimental setup is shown in Fig. 1 and is typical of those used in photo-initiated pulsed chemical lasers.^[18,21] The gases are admitted into the reaction volume in succession; the pressure of reacting components of the mixture were in most experiment constant at 22, 74, and 37 Torr for H_2 , F_2 , and O_2 , respectively. The O_2 was used to stabilize the reaction mixture.^[22]

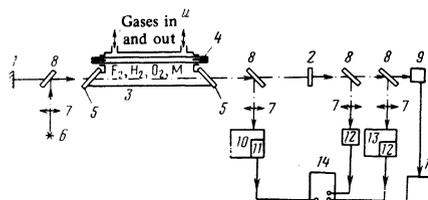


FIG. 1. Experimental setup: 1—total-reflection mirror, 2—output mirror, 3—laser cell, 4—photolytic flash lamp, 5—fluorite windows, 6—IFP-800 flash lamp, 7—lens, 8—deflecting plate, 9—calorimeter, 10—ZMR-3 calorimeter, 11—FÉU-39 photomultiplier, 12—IR-radiation detector, 13—IKM-1 monochromator, 14—S1-42 oscilloscope, 15—potentiometer.

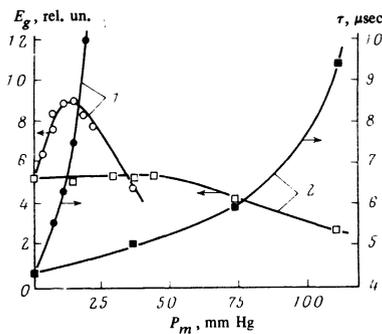


FIG. 2. Laser generation energy (o, □) and explosion delay (●, ■) vs. the dilution of the mixture with molecules C_5F_{12} (1) and O_2 (2).

The chemical reaction was initiated by the pulsed light source (duration $\sim 5 \mu\text{sec}$) described in^[23]. The $H_2 + F_2$ reaction was initiated in the experiments by explosion.^[20] The procedure described in^[24] was used to measure the delay of the explosion at a depth of $\sim 15\%$ of the transformation.¹⁾ In accordance with the known reaction mechanism, there is a one-to-one connection between the delay of the explosion (τ) and the rate of the chemical reaction at $t = \tau$ (this fact can be easily traced also on the obtained oscillograms). The delays were measured at a depth $\sim 15\%$ of the transformation because under our conditions the maximum lasing intensity was observed in this region. The measured explosion delay served thus as a measure of the chemical reaction in the lasing process.

The resonator used in the experiments consisted of a flat metallic mirror and a ZnSe plate. The purities of the employed gases were 99.5%, 98%, and 99.4% for H_2 , F_2 , and O_2 , respectively; the C_2F_6 was analyzed for the HF content, and its concentration turns out to be less than 0.3%. The generation spectra of a number of experiments were obtained by the procedure of Greiner *et al.*^[25] The waveform of the total radiation pulse and the waveforms of the lasing pulses in individual lines were recorded with IR detectors based on gold-doped germanium and with an IKM-1 monochromator.

RESULTS AND DISCUSSIONS

The principal experimental results are shown in Figs. 2 and 3. Figure 2 shows plots of the lasing energy and

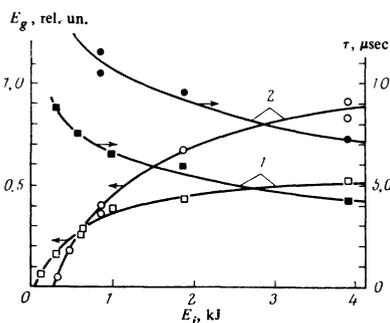
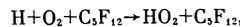


FIG. 3. Lasing energy (o, □) and explosion delay (●, ■) vs initiation energy for mixture without C_5F_{12} (1) and with 15 Torr C_5F_{12} (2).

of the explosion delay time for an $H_2-F_2-O_2$ mixture (22, 74, and 37 Torr, respectively) on the C_5F_{12} pressure (curves 1) and on the O_2 pressure (curves 2) without C_5F_{12} molecules. The initiation energy was constant at 4 kJ. It is seen from Fig. 2 that when the C_5F_{12} mixture is added the lasing energy first increases, and then reaches a maximum and decreases (the rate of the chemical reaction (as revealed by the explosion delay) decreases monotonically).

We note that the increase of the lasing energy with simultaneous delay of the rate the chemical reaction contradicts the known concepts concerning the connection between the lasing energy and the rate of the chemical reaction.^[18,19] The lasing energy at the maximum increased by 1.8 time. The decrease of the energy at higher C_5F_{12} concentrations is due to the strong slowing down of the chemical reaction both because the C_5F_{12} molecules break the chains with high efficiency:



and because of the large heat capacity of the C_5F_{12} molecules, which makes for worse conditions of mixture explosion.^[22] If, however, the rate of the reaction at a certain fixed C_5F_{12} concentration is increased by decreasing the O_2 concentration, then the lasing energy is again increased. Nonetheless, we did not succeed in obtaining an energy gain larger than by a factor of 1.8 compared with the mixture without the C_5F_{12} . An increase of the amount of O_2 in the mixture, as expected, has led only to a decrease of the lasing energy.

Figure 3 shows the lasing energy as a function of the initiation energy for two mixture composition—with dilution by C_5F_{12} (15 Torr) and without dilution. The figure shows also the corresponding plots for the explosion delays. It is seen that in the entire investigated interval of the initiation energies the rate of the chemical reaction following addition of the C_5F_{12} is lower than without the addition. In the low initiation-energy region the rate of the reaction with C_5F_{12} becomes so small that the lasing threshold is not reached. At high initiation energies, the effect of the increase of the lasing energy manifests itself clearly in the C_5F_{12} mixture.

Figure 4 shows oscillograms of the lasing pulses without dilution and with addition of 15 Torr of C_5F_{12} to the

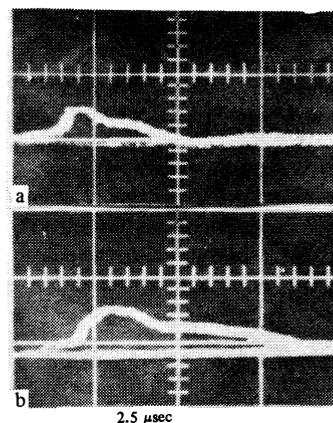


FIG. 4. Laser pulse without C_5F_{12} (a) and with 15 Torr C_5F_{12} (b).

mixture. It is seen from the oscillograms that addition of C_5F_{12} increases the delay of the lasing start, lengthens the radiation pulse, and increases its amplitude. A comparison of the obtained spectra has shown that addition of the C_5F_{12} increases the number of the lines. The transitions that take part in the lasing are those with the smaller rotational quantum numbers. In addition, as shown by experiments on the time development of a number of lines following introduction of C_5F_{12} into the mixture, one can follow the successive appearance of generation lines belonging to a given vibrational transition.

Although the lack of sufficient information concerning the entire aggregate of the relaxation processes it is difficult at present to carry out a complete quantitative analysis of the results, it is possible nevertheless to draw a number of general conclusions. The entire aggregate of the results on the influence of C_5F_{12} on the parameters of $(H_2, F_2)CL$ lasing, in light of the general concepts considered in the introduction, offers evidence of the variation of the "rotational" lasing regime, namely, on a transition to conditions of faster R relaxation.

Let us examine at least semi-quantitatively the causes of the increase of the pulse energy. It is natural here to compare the lasing parameters at equal explosion delays, i. e., at approximately the same kinetics of the chemical process. It is seen from Fig. 3 that at delay times $\tau = 7 \mu\text{sec}$ and $\tau = 9 \mu\text{sec}$ the values of the relative gain of the lasing energy following addition of the C_5F_{12} amount to ~ 3.5 and 4.5 , respectively. These values exceed the maximum calculated ratio of the gain on going from the regime of frozen R relaxation to the instantaneous one. Thus, the result gives grounds for assuming that the introduction of the C_5F_{12} leads to a decrease of the effective rate of the relaxation process, i. e., to an increase in the depth of the chemical transformation at which the lasing ceases.

¹The experimental procedure for simultaneously recording the lasing and the kinetics of the chemical reaction was developed by O. M. Batovskii.

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