HF-CHEMICAL LASER BASED ON HYPOFLUORITE (CF_3OF OR $\text{CF}_2(\text{OF})_2$)-CONTAINING MIXTURES

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The possibility of using fluoro-organic hypofluorites (CF_3OF or $\text{CF}_2(\text{OF})_2$) as a source of atomic fluorine for hydrogen oxidation in the working mixture of HF-chemical lasers, with pulsed CO_2 -laser pumping, was proved theoretically and experimentally. The results suggest an increase of the generation energy due to the chain reaction energy developed in the chemical laser working mixture.

KEY WORDS: Chemical laser, hydrogen fluoride, chain reaction, CO_2 -laser.

The idea of HF-chemical laser development was successfully solved in 1969.¹ However despite such a “mature” age researchers are still attracted by the problems of the development of new mixtures for HF-lasers, especially those which work in chain-reaction mode. Such mode suggests the increase of the generation power and of the efficiency. One of the most significant features providing the operability of a chemical laser is the method of initiation.² By the initiation we mean the way of obtaining fluorine atoms in the working mixture of the laser. One of the possible methods of fluorine atom formation is dissociation of the fluorine-containing molecule. In particular, the bond energy of molecular fluorine is 159.2 kJ/mol. Dissociation may be made by UV irradiation on wavelength $\lambda < 350$ nm. As a result of strong absorption of UV pumping energy in the laser mixture the concentration of fluorine atoms necessary for laser starting will decrease along the excitation area.

IR multiquantum excitation of fluorine-containing molecules may be used as another possible source of photoinitiation.³ In this case the gas volume irradiated with the pumping radiation forms an antireflecting area, which provides uniform initiation of the mixture through the length of the cell.⁴ In this work we use the product of multiquantum dissociation of fluoro-organic hypofluorite molecules (trifluoromethylhypofluorite, CF_3OF , and trifluoromethylene-bis-hypofluorite, $\text{CF}_2(\text{OF})_2$), irradiated with a pulsed CO_2 -laser, as a source of atomic fluorine. The rather weak bond energy of O-F, equal to 182.2 kJ/mol for CF_3OF and 166 kJ/mol for $\text{CF}_2(\text{OF})_2$, makes the above molecules rather attractive for the purpose.⁵ CF_3OF dissociation under excitation with the pulsed CO_2 -laser was shown in,⁶ while $\text{CF}_2(\text{OF})_2$ dissociation was demonstrated in.⁷ Intensive fluorescence of hydrogen fluoride with a maximum at 2.7 μm and that of COF with a maximum at 5.5 μm is observed in the mixture with hydrogen-containing molecule (H_2 , CH_4) due to laser

effect.⁸ As^{6,7} show the dissociation of the molecules studied is as follows:

Atomic fluorine formed in the above reactions initiates the usual scheme of HF-chemical laser reactions:

Vibrationally excited molecules of hydrogen fluoride formed in the above and in the further reactions are the source of fluorescence with a maximum at 2.7 μm . These results allow us to expect hydrogen fluoride molecule generation.

To simplify the calculations let us consider a three-level model of HF-laser, i.e. let us consider the first three vibrational levels of this molecule: a zero, one and two excited levels. The induced transitions in this system possess the highest intensity with rotational quantum number $J = 6$.² Such limitation in the consideration of the frequencies of the induced transitions should not distort the real processes significantly, as laser radiation is the most intense at these levels and starts first in time, according to the experimental results.^{4,9}

As the durations of HF-generation pulse and CO_2 -laser pumping pulse are of similar order of magnitude, the model of instant initiation will not meet the requirements of the problem. Laser dissociation of CF_3OF was approximated by an exponential expression which provided the dissociation of about 10% of the initial substance (experimental results given in^{6,7}) in 1 μsec (CO_2 -laser pulse duration). In 1 μsec the increase of concentrations according to these laws was stopped according to the program.

In our case the generation will take place at frequencies $\nu_{2-1} = 3693.5 \text{ cm}^{-1}$ and $\nu_{1-0} = 3531.2 \text{ cm}^{-1}$ and Einstein coefficients for the induced transitions are $^2 B_{21}(1, 6, -1) = 9.409 \cdot 10^{13} \text{ cm}^2 \text{J}^{-1} \text{ sec}^{-1}$ and $B_{10}(0, 6, -1) = 4.7826 \cdot 10^{13} \text{ cm}^2 \text{J}^{-1} \text{ sec}^{-1}$. Rotational energy of the respective vibrational-rotational condition ($E_{25} = 569.2 \text{ cm}^{-1}$, $E_{16} = 821.2 \text{ cm}^{-1}$, $E_{15} = 591.7 \text{ cm}^{-1}$, $E_{06} = 859.8 \text{ cm}^{-1}$), statistic rotational sum for the respective rotation-vibrational condition ($Q_{\text{rot}}^1 = 11.0$, $Q_{\text{rot}}^2 = 12.0$), Doppler line halfwidth ($\alpha_D(0, 6, -1) = 0.005171 \text{ cm}^{-1}$, $\alpha_D(1, 6, -1) = 0.00489 \text{ cm}^{-1}$), Lawrence line halfwidth ($\alpha_L = 0.003 \text{ cm}^{-1}$), line shape function ($\Phi_{21} = 67.95 \text{ cm}$, $\Phi_{10} = 65.86 \text{ cm}$) were calculated from the known equations.² Gain factor, β , was calculated on the base of the above values.

Laser radiation density was determined from equation

$$\frac{dI_{ik}}{dt} = C \cdot (\beta - \beta_{\text{thres.}}) \cdot I_{ik} \quad (4)$$

Threshold gain factor is calculated from

$$r_1 \cdot r_2 \cdot \exp(2 \cdot l \cdot \beta_{\text{thres.}}) = 1 \quad (5)$$

where r_1 and r_2 — are laser mirror reflection coefficients, respectively.

A system consisting of 27 kinetic equations given in⁸ was used in our calculations. The respective system of differential equations contained unknown values of the

concentrations of the initial molecules of CF_3OF and H_2 , vibrationally excited molecules of CF_3OF^* , H_2^* , HF^* , HF^{**} , COF_2^{**} , radicals of F^* , H^* , CF_3O^* , molecules of final products, COF_2 and HF , as well as those of gas temperatures and laser radiation intensity, W/cm^3 . Integration was made by the Runge-Kutt method. The solution stability was obtained by the automatic step selection, which was $10^{-8} - 10^{-10}$ sec. The calculations were made both for isothermal case and for the gas self-heating due to exothermicity of the reactions.

The condition of the gas self-heating in a cylindric container of an infinite radius length may be expressed as follows 10:

$$\frac{r^2}{\lambda \cdot R \cdot T_0^2} \cdot \sum_i V_i \cdot Q_i \cdot E_i = 2 \quad (6)$$

where λ – is thermal conductivity coefficient, T_0 – is inflammation temperature, V_i – is the rate of a respective reaction with thermal effect Q_i and energy, E_i . As it is known from the kinetic theory of gases when the distance of the molecule free path is much lower than the thickness of heat conducting layer, then λ depends on the pressure. For the pressure value of 1 Torr the distance of the molecule free path, $l = 0.008$ cm, i.e. the 1 cm thick layer will be already large and table values of λ can be used.

Figure 1 shows the results of computations. It follows from eq. (6) that when the temperature of the gas increases significantly the condition of thermal explosion will always be fulfilled. The generation pulse becomes shorter and the power increase is negligible. The used three-level calculation value for HF-laser does not allow to

Figure 1 Calculated shapes of the generation pulse for a chemical laser and gas temperature rise kinetics (pressure ratio 21:9); 1 and 2 – not considering CF_3OF thermal dissociation; 3 and 4 – considering thermal dissociation.

describe inversion decrease due to the gas heating. Calculation without considering chain processes, which corresponds to the substitution of CF_3OF for SF_6 , shows the decrease of the generation intensity and shortening of its duration.

Nonuniformity of the pumping of the chemical laser active area may have a significant effect of the HF-laser output power. The experiments showed that when pressure varied from 2 to 50 Torr then the absorbed energy value in a 39 cm long cell (which corresponds to the length of the laser cell) varied from 0.6 to 2.0 J ($\nu_{\text{las.}} = 931 \text{ cm}^{-1}$, $S = 0.16 \text{ cm}^2$, $\Phi = 7 \text{ J/cm}^2$). Dissociation yield (fluorine atom yield) was also dependent on the gas pressure. We did not manage to obtain experimental data on the CF_3OF dissociation yield for high pressures. Therefore the results for $\text{CF}_2(\text{OF})_2$ molecule dissociation yield were used in the computations. However dissociation yield variation from 10 down to 7% within the respective hypofluorite pressure range from 1 to 21 Torr does not change the chemical laser energy significantly.

The stability of CF_3OF and $\text{CF}_2(\text{OF})_2$ mixtures with oxygen was checked experimentally. It allowed to use standard compositions of HF-chemical laser mixtures with hypofluorite added. CF_3OF ($\text{CF}_2(\text{OF})_2$): F_2 : O_2 : SF_6 : H_2 mixture was used. Almost longitudinal pumping was performed with an excimer XeCl-laser. The experimental results showed that the addition of hypofluorites bring about additional losses in the active medium of the chemical laser, which brings about the decrease of the gain factor, and as a result, the decrease of the laser output energy. Such an effect of polyatomic molecules can be explained by the increase of the relaxation rate of hydrogen fluoride vibrationally excited molecules. Besides, fluorophosgen – the final product of CF_3OF dissociation – also can absorb the excimer laser radiation and thus decrease the rate of the mixture excitation.

Figure 2 shows the schematic diagram of the second experimental unit. Two spherical metal mirrors are used as the chemical laser resonator. The radiation directed out of the resonator with the help of a NaCl plate was fed to the detector input. Pumping was fulfilled by a pulsed CO_2 -laser along the laser cell axis and corresponded to the geometry of a straight beam with 1-cm^2 cross-section at the input and output. To eliminate spurious reflections the cell windows were tilted at low angles. The gas mixture is fed into the cell through 2 inlets which are 27 cm apart for better gas mixing. The mixture was pre-prepared in a balast container and then was fed into the pre-evacuated and fluorine-passivated cell.

Figure 2 The experimental unit schematic diagram: 1, 2 – copper mirrors forming the HF-laser resonator; 3, 4 – rotatable copper mirrors; 5 – cell with the working gas mixture; 6 – rotatable NaCl plate; 7 – filters; 8 – detector.

To check the operability of the laser system HF generation was obtained on $\text{SF}_6 + \text{H}_2$ mixture. Then substitution of SF_6 for hypofluorite was made gradually. The highest intensity of HF-generation was obtained when the working mixture contained one of fluorine-containing molecules. In case of partial disalignment of the resonator generation pulse could be observed on the fluorescent signal background. Blocking one of the mirrors leaves only the fluorescence signal. Figure 3 shows characteristic generation pulses. Change of the laser mixture parameters brings about the pulse shape change as well as delay of the beginning of HF-generation from the moment of pumping pulse.

Addition of 0–25 Torr of Helium into the mixture of $\text{CF}_2(\text{OF})_2$ (14 Torr) + H_2 (6 Torr) resulted first in the increase of the generation intensity more than three times and then in its stabilization and further decrease down to the generation break down. These results demonstrate the effect of thermal processes on the generation. A two-peak structure of the HF-generation pulse obtained on hypofluorite-containing mixtures shows sufficient contribution of the chain processes into the generation energy. The presence of the second peak seems to be due to the chain processes and simultaneous gas temperature rise.

Figure 3 Oscillogram of the chemical laser generation pulses obtained on three various mixtures: left-right 1) $\text{SF}_6:\text{H}_2 = 7:3$; 2) $\text{CF}_2(\text{OF})_2:\text{H}_2 = 7:3$; 3) $\text{CF}_3\text{OF}:\text{H}_2 = 7:3$. Total pressure of the mixture is 5 Torr, scanning – $1\mu\text{sec}/\text{division}$.

Figure 4 HF-generation intensity dependence on fluorine pressure in two laser mixtures under 10 Torr
 1— $\text{CF}_2(\text{OF})_2:\text{H}_2:\text{F}_2:\text{He} - 7:3:\text{F}_2:\text{He}$ 2— $\text{CF}_2(\text{OF})_2:\text{H}_2:\text{F}_2:\text{He} - 7:1:\text{F}_2:\text{He}$.

Generation intensity can increase during feeding fluorine into the mixture due to the initiating of a “hot” reaction for forming vibrationally excited SF_6^* molecules with the help of fluorine molecules¹¹. In our experiments fluorine acted as a buffer gas. Application of hypofluorite as an initial source of fluorine atoms shows that “hot” reaction can be used in this case. However Figure 4 shows that additional work is necessary, aimed at the working gas mixture composition improvement to provide positive fluorine effect.

In conclusion it should be mentioned that the possibility to use the molecules of fluoroorganic hypofluorites (such as CF_3OF and $\text{CF}_2(\text{OF})_2$) as hydrogen oxidizers in the working mixtures of HF-chemical lasers has been proved theoretically and experimentally. The pumping energy in this case is sufficiently lower than in case of SF_6 molecules. The experimental results allow us to hope that the energy of the branched chain reaction will be used for the increase of the chemical laser output energy.

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