

# Processes in chemical lasers

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A review is given of the information on the processes resulting in the formation and loss of population inversion in the most widely encountered types of chemical laser. This information is used to determine the optimal conditions for the excitation of chemical lasers under cw and pulsed conditions.

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## 1. INTRODUCTION

Chemical lasers represent one of the most interesting—in the practical and scientific sense—classes of gas lasers. The practical interest originates from their potential use in material processing, in experiments on the interaction of high-power coherent radiation with matter, in pulsed thermonuclear fusion systems, and in selective interaction with certain degrees of freedom of molecules. On the other hand, chemical lasers are systems whose operation depends on simultaneous occurrence of a variety of physical and physicochemical processes involving vibrationally and rotationally excited molecules, chemically reactive radicals, and rare gas atoms. The foremost among these processes are the simplest exothermal chemical reactions producing vibrationally excited molecules, vibrational relaxation processes, and exchange of vibrational quanta occurring in collisions between such molecules, etc. The mechanism and nature of these processes governs the feasibility of a chemical laser and its optimal operating conditions, and this is why the appearance of chemical lasers has become a powerful factor stimulating investigations of such processes. The consequence of this interest has been rapid accum-

ulation, in the last few years, of information on the qualitative and quantitative characteristics of such processes. For example, detailed experimental and theoretical studies have been made of the dependences of the efficiencies of relaxation and chemical processes on the gas temperature, as well as on the initial and final vibrational states of molecules participating in these processes. Information of this kind is essential not only in connection with the development of chemical lasers, but also in the various important branches of physics dealing with shock waves, combustion and explosions, properties of the atmosphere, etc. A review of this information, whose size, novelty, and rich physical content allow us to regard it as a new branch of physics research, is the main purpose of the present paper. The author hopes that it will interest not only specialists in quantum electronics but also other physicists dealing with vibrationally excited molecules. Data on the formation and loss of vibrationally excited molecules in chemically active gases will be used to analyze the optimal conditions for the excitation of specific laser systems.

The feasibility of direct conversion of chemical energy into the energy of coherent radiation was estab-

lished in principle<sup>1</sup> and confirmed experimentally<sup>2</sup> during the first years of existence of gas lasers, but in the early studies the efficiency of such conversion has been very low. Subsequent intensive investigations and developments, the most important of which have been discussed in recent reviews and monographs,<sup>6-9</sup> have improved greatly the energy parameters of chemical lasers which—alongside with CO<sub>2</sub> and CO lasers—are among the most powerful and efficient among gas lasers. For example, the output power of cw chemical lasers can exceed 100 kW for an efficiency of a few percent.<sup>3</sup> The most efficient pulsed chemical lasers<sup>4</sup> emit up to 4 kJ in 20 nsec when the pump energy is about 7 kJ.<sup>1)</sup> These developments have thus realized the most attractive property of chemical lasers, which is that a considerable proportion of the chemical energy stored in a system can be converted directly and efficiently into laser radiation energy. The most striking manifestation of this property is observed under conditions when the excitation of a chemical laser is by a chain reaction. Then, the energy required to initiate the reaction can be a small fraction not only of the total chemical energy stored in the system but also of the output energy of laser radiation.

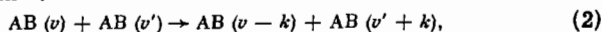
## 2. MECHANISMS OF EXCITATION OF CHEMICAL LASERS

Research on and development of chemical lasers have been concerned mainly with the systems utilizing vibrational-rotational transitions in diatomic molecules. Such molecules are excited by the simplest exothermal reaction



here, AB is a diatomic radical, and R is a residual which can be a single atom or a polyatomic radical. The most interesting case is that of a chain reaction which occurs when radicals formed by the reaction (1) participate in new reactions that produce the B radicals again. Table I lists the parameters of some diatomic molecules and radicals used as active media or initial components of chemical lasers.<sup>5</sup>

The energy  $\Delta E$  evolved as a result of exothermal reactions of the (1) type is distributed among various degrees of freedom of the reaction products in a manner far from equilibrium. In the majority of such reactions the proportion of the energy transferred to the vibrational degrees of freedom of the AB molecules is several times greater than the equilibrium value. Collisions of the resultant vibrationally excited molecules are accompanied by resonant exchange of vibrational quanta:



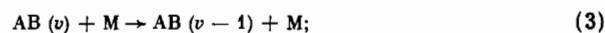
which establishes a quasiequilibrium distribution of molecules between the vibrational states. This pro-

<sup>1)</sup> Estimates<sup>4</sup> demonstrate that the pump energy introduced directly into the active medium of a laser does not exceed 2.5 kJ. The commonly used indicator of the efficiency of utilization of the pump energy in initiation of a chemical laser is known as the electrical efficiency, whose value in this case exceeds unity.

TABLE I. Parameters of diatomic molecules suitable for chemical lasers<sup>5</sup>.

Molecule	Binding energy, kcal/mole, eV		Vibrational quantum $\omega_e$ , cm <sup>-1</sup>	Anharmonicity $\omega_e x_e$ , cm <sup>-1</sup>	Probability of spontaneous emission $A_{10}$ , sec <sup>-1</sup>	Rotational constant $B$ , cm <sup>-1</sup>
H <sub>2</sub>	113.3	4.48	4397	118	0	60.81
D <sub>2</sub>	105.1	4.55	3118	64.1	0	30.43
T <sub>2</sub>	105.9	4.59	2524	43.9	0	20.32
F <sub>2</sub>	37	1.60	924	16	0	0.80
Cl <sub>2</sub>	57.2	2.48	564.9	4	0	0.24
Br <sub>2</sub>	45.4	1.97	323.21	1.03	0	0.08
I <sub>2</sub>	35.6	1.54	214	0.607	0	0.037
HF	135	5.86	4141.03	90.44	194	20.94
HCl	102	4.43	2990.95	52.82	34.6	10.59
HBr	86.6	3.76	2849.4	42.25	7.2	8.47
HI	70.4	3.05	2308	38.98		6.55
DF	136	5.90	3000	47	54.4	11.0
DCI	103.4	4.48	2144.8	26.9	9.5	5.44
DBr	87.8	3.81	1885	22.73		4.29
DI	71.3	3.19	1640	21.16		3.3
CO	256.2	11.11	2170	13.46	33.4	1.93
O <sub>2</sub>	118	5.115	1580	12.1	0	1.446
CS	169.6	7.35				
SO	123.6	5.36	1124	6.12		0.709

duces a strongly nonequilibrium molecular gas of diatomic AB molecules in which the energy per vibrational degree of freedom is considerably greater than the corresponding values for the translational and rotational degrees of freedom. Such a nonequilibrium gas is a ready-made active medium in which a large number of vibrational-rotational transitions of the P branch ( $j - j + 1$ ) of the ground electron state of the AB molecules exhibits a population inversion (Refs. 10-12).<sup>2)</sup> The feasibility of using such an active medium in a chemical laser and the output characteristics of such a laser depend on the rate of formation of vibrationally excited molecules as a result of the chemical reaction (1) and the rate of deexcitation of such molecules by vibrational relaxation:



here, M is an atom or a molecule which is present in an active laser medium and  $v$  is the number of a vibrational level.

We can thus see that the mechanisms of excitation of chemical lasers include initiation of a chemical reac-

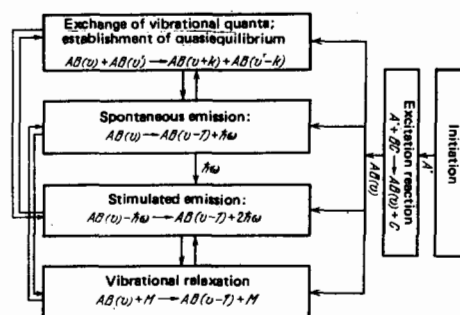


FIG. 1. Mechanisms of excitation of chemical lasers.

<sup>2)</sup> The properties of nonequilibrium molecular gases with a large difference between the vibrational and translational temperatures are now being investigated intensively. We cannot deal in detail with this problem, which is of considerable importance for chemical lasers; the interested reader may consult detailed publications<sup>13-20</sup> where a very full bibliography can be found.

tion, which produces chemically active free radicals, and processes described by Eqs. (1)–(3) that determine the magnitude and nature of a population inversion and its lifetime. The processes involved in the excitation of a chemical laser are shown schematically in Fig. 1. The various types of chemical laser differ from one another by the composition of the active medium, initiation method, and relative importance of the collisional processes (2) and (3).

### 3. REACTIONS RESULTING IN EXCITATION OF CHEMICAL LASERS

#### a) Characteristics of reactions

We shall consider here the chemical lasers excited as a result of exothermal exchange reactions of the (1) type. The main parameters which determine the feasibility of using some particular exothermal chemical reaction as the basis for the excitation of a laser are the values of the rate constant  $K$ , exothermal heat  $\Delta E$ , and fraction of the energy  $f_v$  transferred to the vibrational degrees of freedom of a molecule which is a reaction product. Table II gives the values of these parameters for some of the most widely investigated reactions of this type. We can see that exothermal reactions whose energy is transferred mainly to the vibrational degrees of freedom of the products are a rule rather than an exception. This feature of many exothermal reactions is due to the following circumstances.<sup>56</sup> When reactions of this type occur the electron state of a system becomes modified at large (compared with the equilibrium internuclear separation) distances between colliding particles. The redistribution of atoms is then a fast process which takes a time less than or of the order of a characteristic rotation period of a molecule. Since the internuclear separation in a molecule formed as a result of a transition is greater than the corresponding equilibrium value, such a molecule is in a strongly excited vibrational state and, therefore, the interaction time is too short for the distribution of the vibrational energy between other degrees of freedom.

The most typical and the most important, from the point of view of chemical lasers, example of reactions of this type are the reactions between halogen atoms and a molecule of hydrogen or deuterium or the reactions of a hydrogen atom with halogen molecules. In view of the strong electron affinity of the halogens, an electron "leaks" from a hydrogen to a halogen atom when the distance between the colliding particles is still large; the process is



or



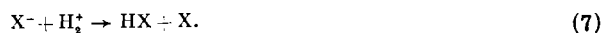
The resultant strong Coulomb attraction between oppositely charged hydrogen and halogen ions breaks the covalent chemical bond in an  $X_2$  ( $H_2$ ) molecule and produces a stronger ionic bond:



or

TABLE II. Parameters of some exothermal exchange reactions.

Reaction	T, °K	Rate constant K, 10 <sup>-13</sup> cm <sup>3</sup> /sec	Energy defect ΔE, kcal/mole	f <sub>v</sub>	Ref.
F + H <sub>2</sub> → HF + H	300	18	33.7	—	21
	300	25	ditto	—	22
	300	25	" "	—	23
	300	—	" "	0.69	24
	300	3.1	" "	—	24
	300	17	" "	—	25
	300	—	32.1	0.72	26
	300	—	ditto	0.74	27
	300	3.8	" "	0.68	28
	300	—	" "	0.82	29
	300	—	" "	0.75	30
	300	—	" "	0.59	41
	300	16.5	—	—	32
	300	1.4	—	—	33
	300	6.3	—	—	34
F + D <sub>2</sub> → DF + D	300	—	31.5	0.66	34
	300	—	31.2	0.66	35
	300	—	—	0.76	34
	300	15.8	—	—	28
	300	—	—	0.59	28
	300	—	31.9	0.65	28
	300	—	ditto	0.75	28
	300	11	—	—	29
	300	21.2	—	—	28
	300	2.6	—	—	27
F + HD → HF + D	300	—	31.9	0.76	27
	300	—	31.2	0.74	27
	300	—	31.2	0.81	28
	300	—	31.2	0.64	28
F + HD → DF + H	300	—	32.8	0.72	27
	—	—	ditto	0.76	29
	—	—	ditto	0.60	26
F + HJ → HF + J	300	—	44.8	0.95	55
F + HBr → HF + Br	300	—	48.5	0.24	37
H + F <sub>2</sub> → HF + F	300	—	97.9	0.53	38
	—	3.7	ditto	—	25
	—	4.3	" "	—	25
	—	—	" "	0.54	39
D + F <sub>2</sub> → DF + F	300	—	99.3	0.56	40
H + Cl <sub>2</sub> → HCl + Cl	300	12	45.2	0.46	42
	300	30	ditto	—	43
	300	—	45.1	0.39	43
D + Cl <sub>2</sub> → DCl + Cl	300	—	46.3	0.39	43
Cl + H <sub>2</sub> → HCl + H	300	—	1.1	0.37	40
Cl + H <sub>2</sub> (v=1) → HCl + H	300	—	7.15	0.57	40
H + I <sub>2</sub> → HI + I	600	110	42	0.64	44
	700	23	ditto	—	45
H + Br <sub>2</sub> → HBr + Br	300	—	41.2	0.55	34, 46
Cl + HJ → HCl + J	300	—	31.7	0.71	34, 46
Cl + DJ → DCl + J	300	—	31.7	0.71	47
Br + HJ → HBr + J	300	70	32	—	47
	300	11	16.5	—	47
Cl + HBr → HCl + Br	300	—	16.2	0.5–0.6	34
F + CF <sub>3</sub> H → HF + CF <sub>2</sub> H	300	0.15	15.5	0.5	35
F + CH <sub>4</sub> → HF + CH <sub>3</sub>	300	—	34.5	0.60	24
F + C <sub>2</sub> H <sub>6</sub> → HF + C <sub>2</sub> H <sub>5</sub>	300	—	39.0	0.62	24
F + CH <sub>3</sub> C(CH <sub>3</sub> ) <sub>3</sub> → HF + CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	300	—	38.0	0.56	24
F + CH <sub>3</sub> Cl → HF + CH <sub>2</sub> Cl	300	—	37.0	0.68	24
F + CH <sub>2</sub> Cl <sub>2</sub> → HF + CHCl <sub>2</sub>	300	—	38.0	0.51	24
F + CH <sub>3</sub> Br → HF + CH <sub>2</sub> Br	300	—	35.9	0.67	24
F + CH <sub>3</sub> CF <sub>3</sub> → HF + CH <sub>2</sub> CF <sub>3</sub>	300	—	33.5	0.67	24
F + CH <sub>3</sub> Si(CH <sub>3</sub> ) <sub>3</sub> → HF + CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub>	300	—	40.0	0.50	24
F + c-C <sub>6</sub> H <sub>12</sub> → HF + C <sub>6</sub> H <sub>11</sub>	300	—	42.9	0.53	24
F + HCCL <sub>3</sub> → HF + CCL <sub>3</sub>	300	—	42.0	0.37	24
O + CS <sub>2</sub> → SO + CS	300	2.8	21.6	—	49
	300	3.5	ditto	—	50
O + CS → SO + S	300	14.2	76.5	0.95	49
	300	14.3	85.0	0.8–0.95	9
	300	35	ditto	—	9
S + O <sub>2</sub> → SO + O	300	2.2	5.6	—	49
	300	2	ditto	—	50
O + CS <sub>2</sub> → OCS + S	300	0.32	53.9	—	49
	300	2.7·10 <sup>-4</sup>	31.1	—	9
O + CS <sub>2</sub> → CO + S <sub>2</sub>	300	0.35	79.1	—	49
SO + O <sub>2</sub> → SO <sub>2</sub> + O	300	2.6·10 <sup>-3</sup>	12.4	—	49
	300	1.5·10 <sup>-3</sup>	12.8	—	9
CS + SO → OCS + S	300	0.085	38.7	—	49
O + OCS → CO + SO	300	0.014	95.9	—	49
	300	0.017	51.4	—	9
S + CS <sub>2</sub> → CS + S <sub>2</sub>	300	0.22	4.6	—	49
	300	0.12	-1.6	—	9
CS + O <sub>2</sub> → OCS + O	300	5·10 <sup>-7</sup>	42.2	—	49
CS + O <sub>2</sub> → CO + SO	300	70	79	—	7
	300	0.0033	90	—	7
O + NO <sub>2</sub> → NO + O <sub>2</sub>	300	2.0	46	—	7
2SO → SO <sub>2</sub> + S	—	—	7	—	7
SO + NO <sub>2</sub> → NO + SO <sub>2</sub>	—	8.4	57	—	7
O + S <sub>2</sub> → SO + S	300	—	23	—	7
SO + CS → CO + S <sub>2</sub>	300	6.7	22.1	—	7
	—	—	57	—	7
	300	0.0017	62	—	7



The main source of information on the dependence of the rate constant of such an exothermal reaction on the vibrational quantum number of the resultant molecule

TABLE III. Partial rate constants of exothermal reactions producing molecules in vibrational state of given number  $v$  (rel. units).

Reaction	$v=0$	1	2	3	4	5	6	7	8	9	10	Ref.
$F + H_2 \rightarrow HF + H$	—	0.31	1.0	0.47	0	—	—	—	—	—	—	34
$F + CH_3C(CH_3)_2 \rightarrow HF + CH_2C(CH_3)_2$	—	0.29	1.0	0.51	—	—	—	—	—	—	—	58
$F + CH_3Cl \rightarrow HF + CH_2Cl$	—	0.35	1.0	0.45	0	—	—	—	—	—	—	51
$F + CH_2Cl_2 \rightarrow HF + CHCl_2$	—	0.31	1.0	0.50	0	—	—	—	—	—	—	24
$F + CH_2Br_2 \rightarrow HF + CH_2Br_2$	—	0.28	0.65	1.0	0.71	—	—	—	—	—	—	34
$F + CH_3CF_3 \rightarrow HF + CH_2CF_3$	—	0.39	1.0	0.24	—	—	—	—	—	—	—	24
$F + CH_3Si(CH_3)_3 \rightarrow HF + CH_2Si(CH_3)_3$	—	0.32	1.0	0.95	—	—	—	—	—	—	—	24
$F + c-C_6H_{12} \rightarrow HF + C_6H_{11}$	—	0.87	0.76	1.0	—	—	—	—	—	—	—	24
$F + HCl_3 \rightarrow HF + ClCl_2$	—	0.44	0.78	1.0	—	—	—	—	—	—	—	24
$F + C(CH_3)_4 \rightarrow HF + C(CH_3)_3CH_3$	—	0.32	1.0	0.27	—	—	—	—	—	—	—	24
$F + C_2H_5OH \rightarrow HF + C_2H_5O$	—	0.51	1.0	0.19	—	—	—	—	—	—	—	24
$F + C_2H_5CH_3 \rightarrow HF + C_2H_5CH_2$	—	0.22	1.0	0.34	—	—	—	—	—	—	—	24
$F + C_2H_4 \rightarrow HF + C_2H_3$	—	1.0	0.80	0.37	—	—	—	—	—	—	—	45
$F + C_2H_6 \rightarrow HF + C_2H_5$	—	0.23	1.0	0.19	—	—	—	—	—	—	—	45
$F + C_2H_2 \rightarrow HF + C_2H$	—	0.72	1.0	0.79	0.07	—	—	—	—	—	—	45
$F + C_2H_4 \rightarrow HF + C_2H_3$	—	—	—	1.0	0.09	—	—	—	—	—	—	48
$F + C_2H_6 \rightarrow HF + C_2H_5$	—	1.0	0.45	—	—	—	—	—	—	—	—	48
$F + CH_3CN \rightarrow HF + CH_2CN$	—	1.0	0.85	0.73	—	—	—	—	—	—	—	48
$F + C_2H_5OH \rightarrow HF + C_2H_5O$	—	1.0	0.36	0.1	0.02	—	—	—	—	—	—	48
$F + C_2H_4 \rightarrow HF + C_2H_3$	0.8	1.0	—	—	—	—	—	—	—	—	—	48
$F + CH_4 \rightarrow HF + CH_3$	—	0.34	1.0	0.2	—	—	—	—	—	—	—	21
$F + C_2H_6 \rightarrow HF + C_2H_5$	—	0.4	1.0	0.14	—	—	—	—	—	—	—	51
$F + C_2H_2 \rightarrow HF + C_2H$	—	0.34	1.0	0.73	—	—	—	—	—	—	—	51
$F + C_2H_4 \rightarrow HF + C_2H_3$	—	0.28	1.0	0.72	—	—	—	—	—	—	—	24
$F + NH_3 \rightarrow HF + NH_2$	—	1.0	0.7	—	—	—	—	—	—	—	—	51
$Cl + HI \rightarrow HCl + I$	—	1.0	0.89	—	—	—	—	—	—	—	—	24
$Cl + HI \rightarrow HCl + I$	—	0.22	0.35	1.0	0.74	—	—	—	—	—	—	34
$Cl + DI \rightarrow DCl + I$	—	0.08	0.14	0.35	0.73	1.0	—	—	—	—	—	34
$H + F_2 \rightarrow HF + F$	0.08	0.10	0.12	0.2	0.5	0.95	1.0	0.56	0.2	0.08	—	41
$D + F_2 \rightarrow DF + F$	0	0	0	0.2	0.5	0.95	0.5	0.02	0	0	—	40
$H + Cl_2 \rightarrow HCl + Cl$	—	0.12	0.13	0.25	0.35	0.78	1.0	0.4	0.26	0.16	—	37
$H + Cl_2 \rightarrow HCl + Cl$	0	0	0	0	0	0.2	0.3	0.55	1.0	0.08	0	40
$H + Cl_2 \rightarrow HCl + Cl$	0	0.28	1.0	0.92	0.1	1.05	1.005	—	—	—	—	42
$H + Cl_2 \rightarrow HCl + Cl$	0	0.01	0.65	1.0	0.4	0	0	—	—	—	—	40
$H + Br_2 \rightarrow HBr + Br$	0	0.4	0.7	1.0	0.2	0.02	0	—	—	—	—	53
$H + I_2 \rightarrow HI + I$	0	0.1	0.3	1.0	0.9	0.3	0.006	—	—	—	—	43
$H + Br_2 \rightarrow HBr + Br$	0	0.03	0.18	1.0	0.99	0.2	0.002	—	—	—	—	43
$H + I_2 \rightarrow HI + I$	0	0.04	0.04	0.42	1.0	0.19	0	0	—	—	—	44, 45

is provided by experimental investigations. Some information of this kind is presented in Table III and in Fig. 2.

We can see that a typical form of a vibrational distribution of the molecules formed as a result of such a reaction can be described by a nonmonotonic curve with a fairly steep maximum at  $v=v^*$ , where  $v^*$  is a vibrational state whose energy is governed by the vibrational energy evolved in the course of the reaction:

$$\hbar\omega v^* \approx f_v \Delta E.$$

We must bear in mind that the distribution of the energy evolved as a result of an exothermal reaction between the degrees of freedom of the product molecules depends largely on the kinetic energy of the particles participating in the reaction. Since an increase in the relative energy of collisions increases the possibility of close approach between molecules or atoms, we can expect the relative importance of this exchange reaction mechanism to decrease on increase in this energy.

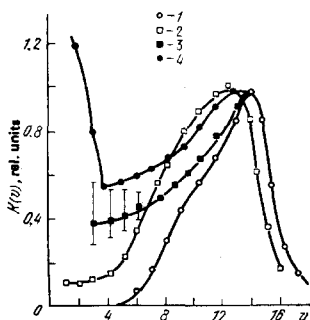


FIG. 2. Distribution of CO molecules between vibrational states after the reaction  $CS + O \rightarrow CO + S$ : 1) Ref. 58; 2) Ref. 59; 3) Ref. 60; 4) Ref. 61.

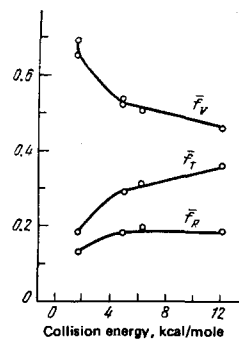


FIG. 3. Dependences on the collision energy of the proportions of the energy transferred to the vibrational ( $f_v$ ), rotational ( $f_R$ ), and translational ( $f_T$ ) degrees of freedom of products of the reaction  $Cl + HI \rightarrow HCl + I$ .<sup>62</sup>

Consequently, the proportion of the energy  $f_v$  transferred to the vibrational degrees of freedom should decrease, whereas the values of the parameters  $f_R$  and  $f_T$  should increase. This is illustrated in Fig. 3, which gives the temperature dependences of the parameters  $f_v$ ,  $f_R$ , and  $f_T$  determined for the reaction  $Cl + HI \rightarrow HCl + I$  in Ref. 62. A similar result was reported in Ref. 63, where an increase in temperature shifted the distribution of the products of the reaction  $F + H_2 \rightarrow HF + H$  between the vibrational states toward lower states. The importance of this feature of exothermal reactions is associated with the fact that the kinetic energy of atoms or radicals participating in chemical reactions depends on the method of formation of these particles and also on the composition of the active medium of a given laser.

We can see from the above discussion that the class of exothermal reactions whose products are characterized by a strongly nonequilibrium distribution of the energy between the various degrees of freedom is very extensive. The reactions for which  $f_v$  exceeds its equilibrium value (in the classical limit this value is  $2/7 \approx 0.285$ , whereas in reality it is even less) are potentially useful in lasers, but one needs additionally a favorable combination of such factors as fast initiation of the reaction in question and a relatively small role of undesirable relaxation processes.

### b) Mechanisms of reaction initiation

Reactions producing vibrationally excited molecules must be initiated, i.e., the original mixture must have a certain number of free radicals capable of participating in the selected reaction. Formation of such radicals is one of the main processes in a chemical laser which determine its construction and output characteristics. Chemical lasers are initiated by all the processes that destroy stable molecules and produce free radicals. We shall now consider these processes and compare their characteristics, which determine the feasibility of using a particular reaction-initiation method in laser systems.

1) *Photoinitiation.* In this case we can expect free radicals as the result of photodissociation of molecules illuminated with a source of visible or ultraviolet radiation:



The most effective mechanism of photodissociation of molecules involves formation of an electronically ex-

cited state characterized by a repulsive term. A molecule which assumes this state as the result of absorption of a photon then dissociates spontaneously acquiring an additional kinetic energy. In this mechanism the energy of a photon necessary to dissociate a molecule may considerably exceed the energy of a bond broken by this process. By way of example, Fig. 4 shows the dependence of the photodissociation cross section of the  $F_2$  molecule on the frequency of the incident photons.<sup>64</sup> We can see that the energy of 4 eV corresponding to the maximum cross section of the process is considerably greater than the binding energy of the  $F_2$  molecule which is  $\approx 1.4$  eV. This circumstance limits the efficiency of photodissociation when this process is used to produce free radicals in active media of chemical lasers.

Another circumstance which enables efficient photo-initiation of chemical lasers is related to the properties of the light source employed for this purpose. Ultraviolet sources used most frequently for this purpose have spectra close to that of a black body. The optimal (from the point of view of utilization of the ultraviolet radiation energy) is a source with a maximum in the emission spectrum coinciding with the maximum of the absorption spectrum of the investigated molecule. For example, in the photodissociation of the  $F_2$  molecule the temperature characterizing the emission spectrum of the photodissociation source should be about 1.5 eV. The maximum efficiency of the utilization of the ultraviolet radiation, estimated with the aid of the appropriate overlap integral, is then close to 25%. Bearing in mind that the photon energy needed for the dissociation of the  $F_2$  molecule is approximately three times greater than the binding energy, we find that no more than 10% of the lost energy is utilized in the photodissociation process. Under practical conditions when, on the one hand, it is difficult to ensure technically that the maxima of the emission spectrum of the source and the absorption spectrum of the molecule coincide and, on the other, the degree of utilization of photons of different wavelengths varies, even less of the available energy is utilized for the purpose in mind.

The efficiency of any given method of initiation of chemical lasers can be defined with the aid of the con-

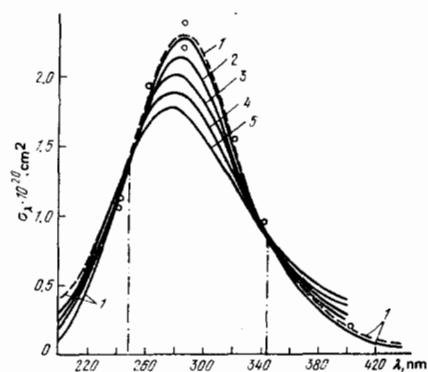


FIG. 4. Dependences of the photodissociation cross section of a molecule on the wavelength of the incident photons at various gas temperatures  $T$  (°K): 1) 300; 2) 510; 3) 660; 4) 800; 5) 990. Results taken from Ref. 64.

cept of an energy "price" of an atom or a radical. In the case of photodissociation of the  $F_2$  molecule by blackbody radiation the minimum price of an atom is 7 eV.

Extensive opportunities for the photoinitiation of chemical lasers are illustrated by the results in Table IV (Ref. 65), which lists the laser transitions in the HF molecule that occur in the process of the  $F + H_2 \rightarrow HF + H$  reaction. Fluorine atoms are formed as a result of photodissociation of various molecules containing this element. The source of initiating radiation employed in such cases is in the form of a flashlamp of the type described in Ref. 66. The laser emission spectrum and the distribution of the reaction products between the vibrational states are largely governed by the nature of the substance containing fluorine.

2) *Electron beam.* When a beam of fast electrons crosses a dense gas, it slows down mainly because of formation of secondary electrons and these, in turn, lose energy as a result of elastic and inelastic collisions with gas particles. Some of these collisions can dissociate molecules and produce chemically active free radicals. This makes electron beams suitable for the initiation of chemical lasers.

The advantages of the electron-beam initiation method are associated mainly with the ability of fast electrons to penetrate as gas and this can ensure efficient excitation of large volumes of an active medium at a high pressure without departing from homogeneity of the excitation in space and time.

The main shortcomings of the electron-beam initiation method are the complex system of devices necessary in such cases, including measures needed to ensure the safety of the operating personnel, and also a system for connecting the vacuum chamber of an electron accelerator to a chamber filled with a high-pressure active medium. The process of damage to a foil which separates such chambers limits the energy which can be injected into the active medium and it thus de-

TABLE IV. Stimulated emission spectrum of photoinitiated HF laser excited by  $F + H_2 \rightarrow HF + H$  reaction using various molecules containing fluorine<sup>65</sup> (asterisk identifies observed transitions).

Original molecule:	UF <sub>6</sub>	XeF <sub>4</sub>	SbF <sub>5</sub>	MoF <sub>6</sub>	N <sub>2</sub> F <sub>4</sub>	WF <sub>6</sub>	CF <sub>3</sub> I	CF <sub>2</sub> -CFCI	CF <sub>2</sub> -CFBr
Transition									
P <sub>1</sub> - 0	(3)		*						
	(4)	*	*				*	*	*
	(5)	*			*		*	*	*
	(6)	*			*		*	*	*
	(7)	*			*		*	*	*
P <sub>2</sub> - 1	(2)		*			*			
	(3)	*	*		*	*	*	*	*
	(4)	*	*	*	*	*	*	*	*
	(5)	*	*	*	*	*	*	*	*
	(6)	*	*	*	*	*	*	*	*
	(7)	*	*	*	*	*	*	*	*
	(8)	*	*	*	*	*	*	*	*
P <sub>3</sub> - 2	(1)					*			
	(2)					*	*		*
P <sub>3</sub> - 2	(3)	*			*	*	*	*	*
	(4)	*			*	*	*	*	*
	(5)	*			*	*	*	*	*
	(6)	*			*	*	*	*	*

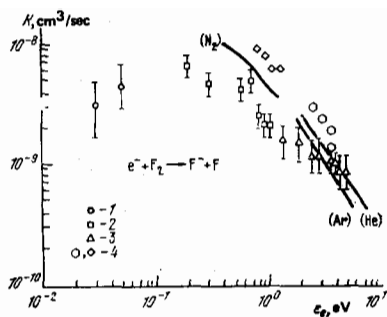


FIG. 5. Values of the rate constant of dissociative attachment of an electron to the  $F_2$  molecule, measured by different authors for different average electron energies: 1) Ref. 67; 2) Ref. 68; 3) Ref. 69; 4) Ref. 70.

termines the output parameters as well as the service life.

The main mechanism of dissociation of molecules containing halogens by electron impact is related to the formation of negative ions, for example,



(dissociative attachment). The electron affinity energy of the fluorine atom (3.45 eV) is considerably greater than the binding energy of the  $F_2$  molecule (1.4 eV), so that the above process is efficient even at low electron energies. Figure 5 shows the results of determinations of the rate constant of this process obtained for various values of the average electron energy.<sup>3)</sup> We can see from these results that the range of electron energies in which the constant of the process is considerably greater than the rate constants of inelastic processes is fairly wide. Therefore, we can assume that all the electrons whose energy is less than a certain value of the order of several electron volts participate in the process of dissociative attachment, which produces a free fluorine atom. An additional fluorine atom is formed as a result of subsequent neutralization of the negative  $F^-$  ion, mainly by charge exchange between the negative and positive ions:



The constant of this process is of the order of  $10^{-6}$  cm<sup>3</sup>/sec (Ref. 56), so that its rate is greater than the rates of all the other processes involving negative ions.

One should point out that the process of dissociative attachment described by Eq. (9) is not the only source of fluorine radicals if a laser is initiated by an electron beam. An experimental study of  $H_2 + F_2$  mixtures strongly diluted with a rare gas (He or Ar) bombarded by a beam of 400 keV electrons in the form of pulses of 50 nsec duration and  $\sim 10$  A/cm<sup>2</sup> current density showed<sup>72</sup> that about four fluorine atoms were produced by each free electron. This was probably due to an additional efficient process of dissociation of the  $F_2$  molecules by electron impact at high (in excess or of the order of 10 eV) electron energies:

<sup>3)</sup> The rate constant of the dissociative attachment of an electron to an  $NF_3$  molecule is  $\approx 2 \times 10^{-11}$  cm<sup>3</sup>/sec for thermal electron energies ( $\sim 300^\circ K$ ).<sup>71</sup>



We can expect a slow electron formed as a result of the above process to participate in dissociative attachment of Eq. (9) before neutralization and this may have the overall result of producing four fluorine atoms. It may occur when an electron which has this energy is not greatly affected by other loss processes, compared with the dissociation process (11). Since the average energy price of an electron formed as a result of the passage of a beam of fast electrons through a dense gas is approximately twice the ionization energy of the gas particles,<sup>12</sup> we find that the price of a fluorine atom in this initiation method is 7–8 eV.

**3) Gas discharge.** When a gas discharge is used, the molecular dissociation mechanisms do not differ greatly from the mechanisms of dissociation by secondary electrons in the course of passage of an electron beam. A discharge with a preliminary ionization by an electron beam or by ultraviolet radiation is particularly effective. The existence of an independent ionization source in this initiation method makes it possible to optimize the electric field intensity so that the same electron is used repeatedly to dissociate molecules. For example, in the experiments described above<sup>72</sup> and involving the use of a high-power electron beam in fluorine dissociation the application of an electric field of intensity up to 15 kV/cm to an  $F_2:H_2:He:Ar$  mixture with a 6:6:54:34 composition at a total pressure of 800 Torr increased the average number of fluorine atoms per secondary electron from four to fifteen. The voltage was about 80% of the breakdown value, so that the electric field produced an optimal (from the energy point of view) electron distribution function. Although the energy price of one fluorine atom ( $\approx 11$  eV) was in this case higher than when an electron beam was used alone, the much higher efficiency of utilization of the secondary electrons reduced the considerable technical difficulties encountered in solving the problem of filling homogeneously a large volume of the active medium with free electrons and of maintaining an electric discharge in a gas with strongly electronegative impurities, such as molecules containing halogen.

**4) Thermal initiation.** In the case of thermal initiation the formation of free radicals is due to thermal dissociation of the original molecules. The efficiency of this method is naturally governed by the binding energy of the resultant radicals and by the specific heat of the original gas. If we consider, as before, the example of formation of fluorine atoms, we find that

TABLE V. Equilibrium degree of dissociation (%) of molecular fluorine at various temperatures and pressures<sup>74</sup>.

p, atm	0.1	0.2	0.4	0.6	0.8	1.0
T, °K						
700	0.5	0.3	0.2	0.2	0.15	0.14
800	2.5	1.8	1.3	1.1	1	0.8
900	9.6	7	5	4	3.5	3.2
1000	26.2	19.3	14.1	11.7	10	9.2
1100	52	41	31.2	26.3	23.3	21.1
1200	77	66	54.1	47.3	42.7	39.4
1300	91	84.5	75.3	69	64	60.4

TABLE VI. Energy required to form a fluorine atom by equilibrium thermal dissociation of an  $F_2$  molecule ( $p = 0.1$  atm).

$T, ^\circ K$	700	800	900	1000	1200	1300	1400
$e_F, eV$	54.6	11.55	3.95	2.04	1.22	1.16	1.15

among the common fluorine compounds the weakest binding is exhibited by the  $F_2$  molecule, for which the binding energy is about 1.4 eV. Table V gives the equilibrium values of the degree of dissociation of the fluorine molecules at various temperatures and pressures.<sup>74</sup> Using the data on the enthalpy of partially dissociated fluorine under the same conditions,<sup>74</sup> we can easily find the energy required to form one fluorine atom. The values of this energy calculated for the pressure of 0.1 atm are listed in Table VI. We can see that from the energy point of view the process of thermal initiation of chemical lasers is very favorable. However, if  $F_2$  is used as the fluorine compound in thermally initiated lasers, serious technical problems are encountered due to, firstly, the high chemical and biological activity of molecular fluorine, secondly, the difficulty of heating this gas rapidly and, thirdly, the high sensitivity of the parameters of a chemical laser to the gas temperature. For these reasons it is usual to employ other fluorine compounds in thermally initiated lasers because although these compounds are less favorable from the energy point of view, they are more convenient from the practical point of view, which is true of the polyatomic molecules  $SF_6$ ,  $MoF_6$ , etc. The most widely used of these is the  $SF_6$  molecule, whose advantages include the ability to store it for a long time, chemical and biological inertness, and low cost of production. However, the energy required to separate a fluorine atom from this molecule by equilibrium heating is approximately an order of magnitude higher than the corresponding value for the  $F_2$  molecule and this is related, on the one hand, to the high binding energy ( $\approx 3.3$  eV) of the fluorine atom and, on the other, to the much higher specific heat of sulfur hexafluoride.

The additional energy losses involved in thermal initiation of chemical lasers are associated with the difficulty of depositing energy effectively in gases containing halogens and characterized by a strong electro-negativity. This circumstance makes it difficult to heat a gas directly by a discharge and makes it necessary to use a buffer gas subjected to a preliminary heating, which is then mixed with the halogen-containing compound causing heating and partial dissociation of the latter. This method of gas heating increases the specific heat of the active mixture and reduces the energy efficiency of the laser. For example, in Ref. 75 the dissociation of  $SF_6$  was produced by mixing of a gas of these molecules with a buffer gas ( $N_2$  or He) heated in a plasmatron to a temperature above 2000°K and the energy supplied to the discharge (per  $SF_6$  molecule) was 8–10 times greater than the binding energy of the fluorine atom. It should be pointed out that subsequent cooling of the partly dissociated molecular gas in order to create an active medium takes place in systems of

this kind as a result of expansion of the gas through a gasdynamic nozzle.

5) *Chemical initiation.* The most natural initiation method for chemical lasers, which follows from their very nature, is chemical. In this case, the formation of the atoms or free radicals necessary for the excitation of a laser is the result of a chemical reaction. However, one then faces very stringent requirements in respect of the rate of the initiating chemical reaction, which should be higher or of the order of the rate of the reaction producing excited particles. Since the rates of the reactions of free radicals are usually very high and correspond approximately to the rate of gas-kinetic collisions, this requirement greatly reduces the range of reactions suitable for initiation of chemical lasers.

The simplest of the reactions producing fluorine radicals is



Figure 6 shows the temperature dependence of the rate constant of this reaction measured by a variety of methods.<sup>76–78</sup> We can see that the values of this rate constant are considerably smaller than the corresponding rate constants of the reactions involving atomic fluorine and producing a population inversion (Table II). For this reason the efficiency of the above reaction in initiation of chemical lasers is low. Vibrationally excited HF (DF) molecules formed as a result of the reaction of atomic fluorine with hydrogen (deuterium) are lost by collisions with one another faster than they accumulate due to the reaction (12). Therefore, this reaction can be employed effectively only in systems in which a vibrationally excited DF molecule transfers its vibrational energy to a  $CO_2$  molecule because the latter is less effectively deexcited by collisions and can therefore be used for laser action (energy-transfer lasing).<sup>6</sup>

6) *Chain reaction.* Much more widely used and more interesting from the practical point of view are those systems in which formation of free radicals necessary for the excitation of a laser is by the same reaction which eventually excites these radicals. We have in mind here a chain reaction, the most important example of which is that of burning of fluorine in hydrogen:

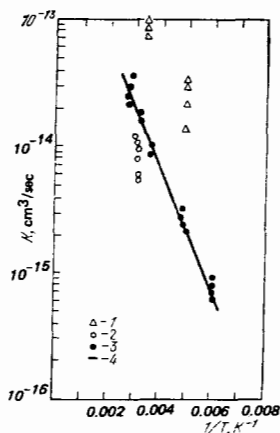
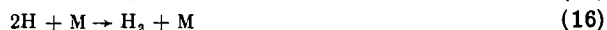


FIG. 6. Temperature dependence of the rate constant of the  $F_2 + NO \rightarrow NOF + F$  reaction obtained in various experiments: 1) Ref. 76; 2) Ref. 77; 3) Ref. 78; 4) dependence  $7 \times 10^{-13} \exp(-1150/T)$   $cm^3/sec$ .



Both stages of this reaction are strongly exothermic so that each of them produces HF molecules mainly in vibrationally excited states (Table II). Breaking of chains, i.e., binding of free radicals, is by exchange recombination of fluorine or hydrogen atoms:

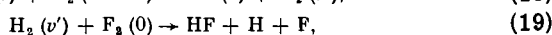
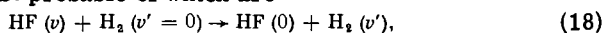


(M is a molecule occurring in the gas), by attachment of hydrogen atoms to oxygen molecules usually present in small amounts in mixtures:



or by loss of radicals on the chamber walls.

In spite of occurrence of these chain termination processes reducing the number of fluorine and hydrogen radicals, the above reaction can under certain conditions be of the branched type (energy branching) so that in the course of this reaction the total number of active centers (F atoms) increases with time. This form of reaction is due to the accumulation of strongly excited HF molecules whose vibrational energy (~3–4 eV) is considerably greater than the dissociation energy of the F<sub>2</sub> molecule. A sequence of processes, the most probable of which are<sup>56</sup>



ensures that the excess energy is used to dissociate molecules and to accumulate active centers.

One should point out that although the number of chain reactions known in chemistry is very large (see, for example, Ref. 56), only a few of these reactions can be used to excite chemical lasers efficiently. One requires a favorable ratio of the rates of accumulation of vibrationally excited molecules and of their collisional deactivation. In this sense the system F<sub>2</sub> + H<sub>2</sub> stands out from among other mixtures capable of chain reaction. The main features of this system are the anomalously high rate constants of the reactions (13) and (14).

We shall conclude this discussion of the initiation methods for chemical lasers by stressing that the energy required to form a radical is not the only (and sometimes not the most important) parameter that governs the advantages and disadvantages of a given initiation method for a specific laser system. The rate of initiation and the ability to excite simultaneously large volumes of an active substance which is at the highest possible pressure are the properties which are important and sometimes decisive. Electric-discharge and electron-beam-controlled initiation methods are characterized by the maximum rate of energy deposition in an active medium. The potentialities of these methods are limited by technical difficulties associated with the creation of high-power electron beams and striking of an electric discharge at a high pressure. The most natural way of overcoming these difficulties is to use a combined discharge in which an electron beam or ionizing ultraviolet radiation creates a cer-

tain number of free electrons in a high-pressure gas and the main excitation energy is introduced by the application of an external electric field in which electrons acquire the energy needed for initiation.

#### 4. RELAXATION PROCESSES IN CHEMICAL LASERS

Collisional processes involving vibrationally excited molecules play an important role in the establishment of a population inversion in a chemical laser. The most important of these processes are those involving exchange of vibrational quanta (2) resulting in a redistribution of the vibrational energy between the various states and also between the various components of the active medium, and vibrational relaxation processes (3) as a result of which the vibrational energy is converted into heat and the inversion is lost. A characteristic property of chemical lasers is that the rate constants of these processes are usually comparable with the rate constants of the chemical reactions used to excite the laser so that processes of formation and loss of a population inversion occur simultaneously and influence one another.

##### a) VT relaxation

In any given situation the role of the VT relaxation processes is governed by the absolute value of the corresponding rate constant and its temperature dependence. In the case of hydrogen halide molecules these two characteristics differ considerably from those of other diatomic molecules. This difference is due to the physical properties of hydrogen halides. For example, the rate constant of the VT relaxation of molecules is governed by the value of the Massey parameter  $a\omega/v$  ( $a$  is the scale length of the change in the intermolecular interaction potential,  $\omega$  is the vibration frequency, and  $v$  is the rate of approach of the colliding molecules).<sup>18,56,79,80</sup> The value of this parameter is usually much greater than unity for diatomic molecules at room temperatures so that the probability of the VT relaxation as a result of thermal collisions is adiabatically small. In the case of hydrogen halides consisting of atoms with very different masses, the Massey parameter is governed not by the approach velocity of the colliding particles but by the rate of rotational motion of the molecules because this faster motion can alter the vibrational state. Naturally, in this relaxation mechanism some of the vibrational energy is transformed into the rotational energy of the molecules<sup>4)</sup> which is then rapidly thermalized. Thus, in the case of hydrogen halides the Massey parameter is approximately  $\sqrt{\mu_1/\mu_2}$  times less than for the molecules consisting of atoms of similar mass ( $\mu_1$  is the reduced mass of a colliding pair and  $\mu_2$  is the reduced mass of a molecule). Consequently, typical values of the rate constant of the VT relaxation process are several orders of magnitude greater than  $\sim 10^{-18} - 10^{-16}$  cm<sup>3</sup>/sec usually found for the majority of diatomic molecules. Table VII lists the room-temperature rate constants of the VT (VR) re-

<sup>4)</sup> For this reason processes of this kind are sometimes called vibrational-rotational (VR) relaxation.



TABLE VII. Rate constants of vibrational relaxation ( $10^{-12}$  cm<sup>3</sup>/sec) of molecules suitable for chemical lasers ( $T \approx 300^\circ\text{K}$ ).

Impurity	HF	H	H <sub>2</sub>	D <sub>2</sub>	F	N <sub>2</sub>	CO <sub>2</sub>
Molecule							
HF	2.2	3 <sup>81</sup> 4.2 <sup>88</sup>	0.63	0.11 <sup>82</sup> 0.09 <sup>84</sup>	100 <sup>85</sup>	0.023 <sup>84</sup>	4.8 <sup>86</sup>
DF	0.8		0.018 <sup>86</sup>	0.64 <sup>86</sup>			
HCl	0.43 <sup>88</sup>	7.7 <sup>81</sup> 6.5 <sup>84</sup> 1.8 <sup>91</sup>	0.004 <sup>89</sup> 0.005 <sup>90</sup> 0.018 <sup>87</sup> 0.017 <sup>89</sup> 0.006 <sup>100</sup> 0.0086 <sup>103</sup>	5·10 <sup>-4</sup> <sup>87</sup>	0.0017 <sup>87</sup> 0.0011 <sup>87</sup>		
DCl							
HBr	0.26 <sup>88</sup>						
DBr				1.3·10 <sup>-5</sup> <sup>87</sup>			
H <sub>2</sub>	10 <sup>-4</sup> <sup>101</sup>		0.03 <sup>104</sup> 2.8·10 <sup>-4</sup> <sup>87</sup>	2.4·10 <sup>-5</sup> <sup>87</sup>			
D <sub>2</sub>							
CS							
Impurity	DF	HCl	He	Ar	Ne	Br	Cl
Molecule							
HF	4.3 <sup>88</sup>						
DF		0.02 <sup>87</sup>	5·10 <sup>-5</sup> <sup>88</sup>	3·10 <sup>-4</sup> <sup>88</sup>	2.5·10 <sup>-5</sup> <sup>88</sup>	0.26 <sup>89</sup>	7 <sup>90</sup> 1.0 <sup>98</sup> 8.3 <sup>99</sup> 3.5 <sup>98</sup>
HCl		0.024 <sup>98</sup>					
DCl			5·10 <sup>-5</sup> <sup>88</sup>	1.8·10 <sup>-4</sup> <sup>88</sup>	8·10 <sup>-4</sup> <sup>88</sup>	0.23 <sup>95</sup> 2.6 <sup>95</sup>	
HBr		0.04 <sup>98</sup>					
DBr							
H <sub>2</sub>							
D <sub>2</sub>							
CS							
Impurity	D	HBr	HD	DF	DBr	CS	
Molecule							
HF							
DF				0.5			
HCl	10.8 <sup>81</sup>		0.0025 <sup>87</sup>	0.45 <sup>88</sup>			
DCl	2.0 <sup>81</sup>		0.008 <sup>87</sup>				
HBr		0.015 <sup>87</sup> 0.016 <sup>88</sup> 0.01 <sup>88</sup>	0.0018 <sup>87</sup>	0.28 <sup>88</sup>			
DBr				0.77 <sup>88</sup>	0.005 <sup>88</sup>		
H <sub>2</sub>						3.4 <sup>105</sup>	
D <sub>2</sub>							
CS							

laxation of diatomic molecules relevant to chemical lasers. In those cases when the results are given without a reference, they are the result of averaging of a large number of similar experimental values. Table VIII gives the rate constants of the vibrational relaxation of the HF molecule in the case of collisions with complex molecules which are sometimes encountered in active media of chemical lasers. It is clear from Tables VII and VIII that the highest values of the VT relaxation constant correspond to collisions of molecules of hydrogen halides with one another and with free radicals (H, F, Cl, Br).

The temperature dependences of the rate constants of the vibrational relaxation of hydrogen halides also differ greatly from the dependences which are typical of the majority of diatomic molecules and are described by the Landau-Teller formula  $k_{VT} \propto \exp(-aT^{-1/3})$  ( $a$  is a parameter).<sup>79</sup> The main reason

TABLE VIII. Rate constants of vibrational relaxation of HF molecules colliding with complex molecules containing hydrogen and fluorine<sup>83</sup>.

Impurity	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	n-C <sub>4</sub> H <sub>10</sub>	cyclo-C <sub>3</sub> H <sub>6</sub>	ClF <sub>3</sub>	CF <sub>4</sub>	NF <sub>3</sub>	SF <sub>6</sub>
$k_{VT}$ , 10 <sup>-14</sup> cm <sup>3</sup>	160	330	410	510	960	350	1.3	0.9	0.15

for this difference is the attraction between the strongly polar hydrogen halide molecules, which is strongest at low temperatures and gives rise to a negative temperature dependence of the relaxation constant at such temperatures. An increase in temperature should reduce the role of attraction and the temperature dependence should become positive. This is confirmed by the results of experimental and theoretical investigations of the rate constant of the process under discussion (Fig. 7).

The nonmonotonic temperature dependence of the rate constants of the VT relaxation of hydrogen halides is important in the operation of chemical lasers. Although the main restriction on the output characteristics of these lasers is associated with the occurrence of undesirable VT relaxation processes, the nonmonotonic temperature dependence of the rate constants of the processes ensures a relatively weak sensitivity of the output parameters to an increase in the temperature of the active medium and, therefore, makes it possible to achieve very high laser output parameters.

Another important property characterizing the relaxation of vibrationally excited molecules of hydrogen halides, which influences the properties of chemical lasers, is related to the dependence of the relaxation rate constant on the serial number of a vibrational state. According to the harmonic oscillator model, which is valid in the case of the majority of diatomic molecules, this dependence is near-linear:  $k_{v,v-1} = \nu k_{10}$ . An important conclusion follows from this linear dependence: the relaxation time of the first vibrationally excited state coincides with the total vibrational energy stores in the system.<sup>126</sup> Experiments indicate that in the case of hydrogen halides the VT relaxation rate constants increase superlinearly with the vibrational state number. This is illustrated in Fig. 8 and in Table IX. The deviation of the dependence  $k_{VT}(v)$  from monotonic behavior, which is observed in some cases, is clearly associated with the exchange of vibrational quanta, whose efficiency depends resonantly on the degree of coincidence of the vibrational quanta of the colliding molecules. Apart from these deviations, the dependence  $k_{VT}(v)$  can in most situations be approximated quite accurately by the power law

$$k_{VT}(v) \sim k_{10}v^n,$$

where the power exponent is  $n \approx 2-3$ .

We must bear in mind that the vibrational relaxation in chemical lasers is a much more serious obstacle than in molecular lasers of other types. The rate of vibrational relaxation is anomalously high in the case of hydrogen halides and it is comparable with the rate of chemical pumping. Therefore, the VT relaxation process not only limits the output parameters of specific laser systems but also determines the optimal composition of the active medium, the main features of the construction of laser systems, and even the feasibility of lasing as a result of any specific chemical reaction.

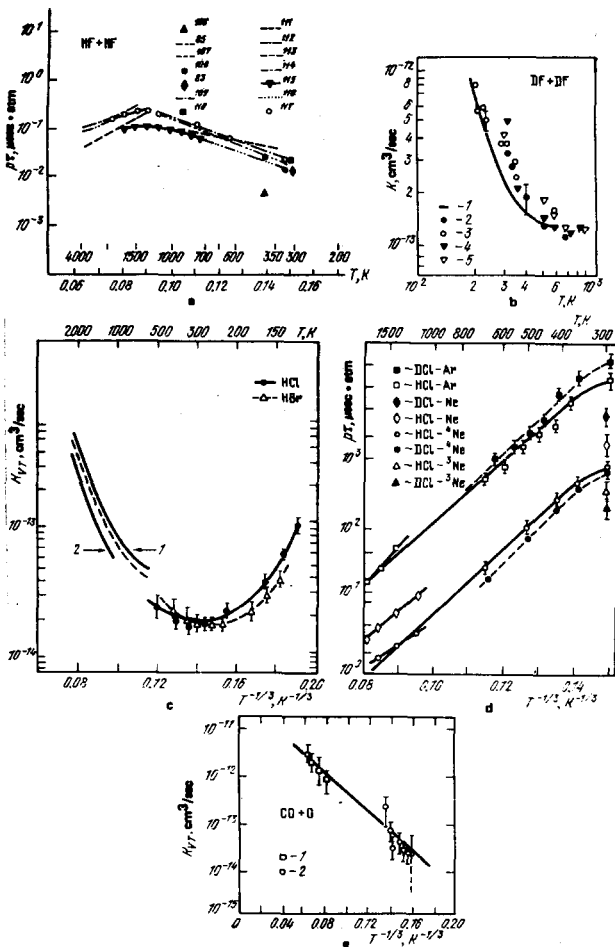


FIG. 7. Temperature dependences of the characteristics of the vibrational relaxation of hydrogen halide molecules: a) HF(1) + HF(0) → 2HF(0) (VT relaxation time at gas pressure of 1 atm); b) DF(1) + DF(0) → 2DF(0), results taken from Ref. 118 (1), Ref. 113 (2), Ref. 120 (3), Ref. 112 (4), Ref. 85 (5); c) HCl, results taken from Ref. 121 (1), Ref. 122 (2), and HBr, results taken from Ref. 87 (1), Ref. 121 (2); d) DCl, HCl mixed with inert gases, results taken from Ref. 88 for  $T < 1000^\circ\text{K}$  and from Ref. 123 for  $T > 1000^\circ\text{K}$ , relaxation time at  $p = 1$  atm; e) CO(1) + O → CO(0) + O, results taken from Ref. 124 (1) and Ref. 125 (2).

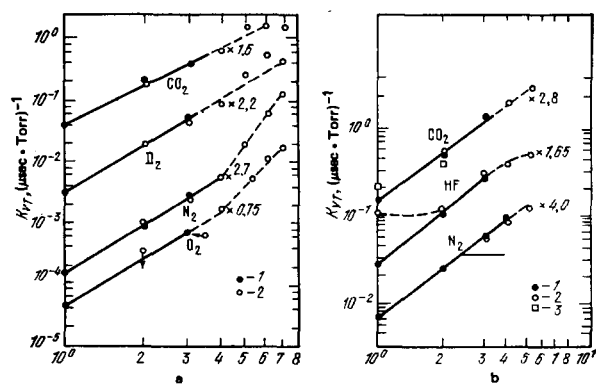


FIG. 8. Dependences of the rate constant of the VT relaxation of vibrationally excited molecules on the vibrational quantum number: a) HF, results taken from Ref. 128 (1) and Ref. 127 (2); b) DF, results taken from Ref. 86 (1), Ref. 127 (2), and Ref. 131 (3). The quenching partner is identified near each curve.

## b) VV exchange

The efficiency of exchange of vibrational energy in collisions between molecules is largely governed by the difference between the energies of the received and lost vibrational quanta. The most effective processes occur when the energies of these quanta are exactly equal (resonant VV exchange), i.e., when the colliding molecules belong to the same type of gas. In the case of accidental equality or a slight difference between the energies of the quanta of molecules of different kind the efficiency of the VV exchange is also sufficiently high for this process to have a significant influence on the redistribution of the vibrational energy in the active medium of a chemical laser. Table X lists the rate constants of the resonant exchange of vibrational quanta for hydrogen halide molecules and for CO. We can see that an increase in the vibrational state number reduces the exchange efficiency because of a reduction in the energy of the transferred quanta as a consequence of the anharmonicity of molecular vibrations.

The dependence of the rate constant of the VV exchange on the difference between the energies of the transferred and received quanta is particularly strong for nonresonant exchange when molecules of different kind collide. These dependences are plotted in Fig. 9 for collisions involving the CO molecule and also for collisions between hydrogen halide molecules of different kinds. We can see that the energy defect is in fact the only parameter that governs the exchange probability.

It is clear from an analysis of the reported results that a typical situation in the active medium of a chemical laser is such that the characteristic times of the VT relaxation and VV exchange processes are of the same order of magnitude as the characteristic time for the formation of a vibrationally excited molecule as a result of a chemical reaction. In this situation a correct estimate of the role of a given process and a reliable calculation of the output parameters of a given system are possible only if accurate information is available on a large number of processes in which vibrationally excited molecules participate. However, the completeness and reliability of such data leaves much to be desired and, therefore, one should treat

TABLE IX. Dependences of rate constants of vibrational relaxation ( $10^{-14}$  cm<sup>3</sup>/sec) of some molecules on vibrational state number in AB( $\nu$ ) + M → AB( $\nu - 1$ ) + M reaction.

Molecule AB	Impurity M	Vibrational State Number $\nu$													Ref.	
		1	2	3	4	5	6	7	8	9	10	11	12	13		
HF	H <sub>2</sub>	43	21 37	15 34	21 47	49	99	16								127 128 129 130
	D <sub>2</sub>		26	59 130	120 330	310	820	610								
DF	H <sub>2</sub>	17.5	6.1	14	29											86
	N <sub>2</sub>	2.3	7.4	16.6 3.5	30 5.7	9.3										88 127
HF	H <sub>2</sub>	112	403	940	630	830										86 131
	CO <sub>2</sub>	481	1840	4700	660	2200	3600									86 127
HCl	D <sub>2</sub>	24	57	48	58											88
	H <sub>2</sub>	0.44	0.88	1.4	1.9											89
CO	He									0.015	0.028	0.034	0.053	0.062		132

with caution the published numerical calculations (see, for example, Chap. 8 in Ref. 9) dealing with tens of different processes.

## 5. CONTINUOUS-WAVE CHEMICAL LASERS

Since a chemical reaction which excites a chemical laser results in irreversible transformations of the original reagents, steady-state (cw) operation of a chemical laser requires a continuous supply of the active medium (circulation). The rate of circulation is governed by two main factors. Firstly, the rate of replenishment of the active medium should be matched to the chemical reaction rate, i.e., in the final analysis it should be matched to the intensity of laser radiation. Secondly, circulation of a gas in a chemical laser prevents accumulation in the active medium of molecules which can cause collisional relaxation of vibrationally excited molecules and, therefore, destroy a population inversion. These factors determine the output parameters and the main characteristics of the construction

TABLE X. Rate constants of resonant exchange of vibrational quanta measured and calculated by various authors for the  $AB(v) + AB(v') \rightarrow AB(v-1) + AB(v'+1)$  reaction.

Molecule	HCl	HCl	HCl	HF	HF	
$v$	1	2	1	3	2	
$v'$	0	0	1	0	0	
$T, ^\circ K$	300	300	300	300	300	
Exchange rate constant, $10^{-12} \text{ cm}^3/\text{sec}$	experiment	19 <sup>132</sup> 8.4 <sup>97</sup>	3.1 <sup>132</sup> 2.8 <sup>133</sup>	4.2 <sup>97</sup>	5.1 <sup>136</sup> 2.0 <sup>137</sup>	25 <sup>136</sup> 19 <sup>137</sup>
	theory	0.7 <sup>134</sup>	0.44 <sup>135</sup>		6.9 <sup>135</sup>	
Molecule	HBr	HBr	CO	CO	CO	
$v$	1	2	1	2	3	
$v'$	1	0	0	0	0	
$T, ^\circ K$	300	300	300	300	300	
Exchange rate constant, $10^{-12} \text{ cm}^3/\text{sec}$	experiment	4.6 <sup>97</sup>	3.0 <sup>97</sup> 4.4 <sup>133</sup>			
	theory		0.09 <sup>135</sup>	2.6 <sup>134, 135</sup> 1.8 <sup>138</sup>	2.8 <sup>138</sup>	4.6 <sup>138</sup> 3.1 <sup>138</sup>
Molecule	CO			CO		
$v$	4	4	4	5	5	5
$v'$	0	0	0	0	0	0
$T, ^\circ K$	100	254	300	100	254	300
Exchange rate constant, $10^{-12} \text{ cm}^3/\text{sec}$	experiment	0.9 <sup>139</sup>	3.2 <sup>139</sup>	2.0 <sup>130</sup>	0.4 <sup>139</sup>	1.8 <sup>139</sup>
	theory		2.4 <sup>98</sup> 3.5 <sup>135</sup>			1.7 <sup>138</sup> 1.2 <sup>135</sup>

TABLE X. (Continued)

Molecule	CO			CO		
	$v$	6	6	6	7	7
$v'$	0	0	0	0	0	0
$T, ^\circ K$	100	254	300	100	254	300
Exchange rate constant, $10^{-12} \text{ cm}^3/\text{sec}$	experiment	0.2 <sup>139</sup>	0.96 <sup>139</sup>	0.63 <sup>130</sup>	0.08 <sup>139</sup>	0.4 <sup>139</sup>
	theory		0.6 <sup>136</sup> 0.55 <sup>135</sup>			0.34 <sup>138</sup> 0.28 <sup>135</sup>
Molecule	CO			CO		
$v$	8	8	8	9	9	9
$v'$	0	0	0	0	0	0
$T, ^\circ K$	100	254	300	100	254	300
Exchange rate constant, $10^{-12} \text{ cm}^3/\text{sec}$	experiment	0.04 <sup>139</sup>	0.2 <sup>139</sup>	0.17 <sup>130</sup>	0.02 <sup>139</sup>	0.1 <sup>139</sup>
	theory		0.16 <sup>138</sup> 135			0.078 <sup>135, 138</sup>
Molecule	CO		CO	CO		
$v$	10	10	10	11		
$v'$	0	0	0	0		
$T, ^\circ K$	100	254	300	100		
Exchange rate constant, $10^{-12} \text{ cm}^3/\text{sec}$	experiment	0.007 <sup>139</sup>	0.055 <sup>139</sup>	0.06 <sup>130</sup>	0.052 <sup>130</sup>	
	theory		0.046 <sup>136, 138</sup>		0.025 <sup>136, 138</sup>	

of cw chemical laser systems. We shall now discuss in detail the most typical laser systems of this kind and analyze optimal operating conditions.

### a) HF laser

The main distinguishing property of this laser, which governs its extremely high output parameters, is as-

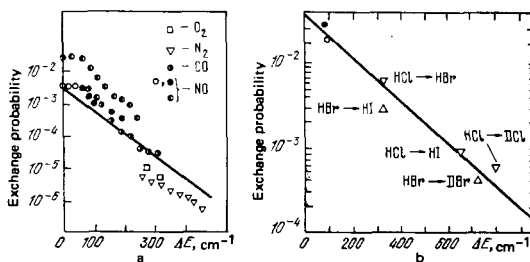


FIG. 9. Dependences of the probability of nonresonant exchange of vibrational quanta in collisions of diatomic molecules on the difference between the energies of these quanta: a) transfer of a quantum from a CO molecule to other molecules<sup>130</sup>; b) collisions of hydrogen halides.<sup>97</sup>

sociated with the anomalously high rate constant of the chemical reaction of burning of hydrogen in fluorine, and also of many exchange reactions which occur between fluorine radicals and various substances containing hydrogen (Table II). The products of these reactions, whose cross sections are close to the gas-kinetic values, are vibrationally excited HF molecules. Another characteristic property of lasers of this type is related to the very high value of the rate constant of the vibrational relaxation of the HF molecules when they collide with one another and with fluorine radicals (Table VII). The rate constant of the first of these processes is only several times less than the rate constant of the chemical reaction (1) producing a population inversion. For this reason the process of vibrational relaxation of the HF molecules has a decisive influence on the output characteristics of this laser, and on the construction of the laser system.

The most commonly used cw HF laser is constructed as follows. Partially dissociated fluorine or a substance containing fluorine is mixed with molecular hydrogen (or a substance containing hydrogen) and is circulated through an optical resonator. A chemical reaction producing vibrationally excited HF molecules occurs inside the resonator. These molecules interact with the resonator field and this gives rise to lasing. The known values of the rate constants of the elementary processes can be used to estimate the optimal parameters and output characteristics of such a system. The time spent by the active medium in the resonator field is limited by the condition that the VT relaxation of the vibrationally excited HF molecules should not be too great during this time. Since the main VT relaxation process is in the form of collisions of the HF molecules with one another and since the transit time obeys the self-evident relationship  $\tau_{tr} = d/v_{tr}$  ( $d$  is the transverse size of the resonator and  $v_{tr}$  is the transit velocity of the molecules), we find that this condition limits the density of the HF molecules in the resonator:

$$N_{HF} \leq \frac{v_{tr}}{dk_{VT}} \quad (20)$$

The above relationship is used to estimate the maximum potentialities of lasers of this type. For example, the maximum laser radiation power  $P_s$  which can be obtained from a unit area of the cross section of the active-medium stream is proportional to the product  $N_{HF}v_{tr}$  and, in accordance with the condition (20), is limited to

$$P_s \leq \frac{v_{tr}^2 h \omega}{k_{VT} d} \quad (21)$$

( $h\omega$  is the energy of a laser radiation photon; it is assumed that each HF molecule formed in this way is used once to obtain stimulated radiation). We can see that the maximum output power of such a laser is largely governed by the velocity of gas circulation through the resonator. The power can be increased radically by using a supersonic nozzle. Such a nozzle is used widely in practical laser systems. The velocity of flow of a mixture through a nozzle can be in-

creased, mixing conditions can be improved, and strong heating of the working medium by the heat due to the chemical reaction can be prevented by diluting the mixture with a large amount of an inert gas (usually helium or nitrogen). We shall now estimate the maximum power of laser radiation per unit area of the throat cross section of a nozzle  $P_s$  in the case when the diluent is helium. If we assume that  $v_{tr} = c_s \approx 10^5$  cm/sec (velocity of sound in helium),  $d \sim 1$  cm,  $k_{VT} \approx 2 \times 10^{-12}$  cm<sup>3</sup>/sec, and  $h\omega \approx 7 \times 10^{-20}$  J, we find that  $P_s \lesssim 300$  W/cm<sup>2</sup>.

The density of the substance containing hydrogen  $N_{RH}$  in the chemical reaction zone can be found from the condition that the rate of accumulation of active molecules as a result of the relevant reaction is greater than the rate of deactivation of these molecules by collisions. Otherwise, the process of deactivation prevents accumulation of vibrationally excited molecules in an amount sufficient for lasing. This requirement can be formulated in the form

$$N_{HF}k_{VT} \leq N_{RH}k_{RH} \quad (22)$$

where  $k_{RH}$  is the rate constant of the  $F + RH \rightarrow HF + R$  reaction that excites the laser. When molecular hydrogen is used ( $RH \equiv H_2$ ), it follows from the condition (22) that

$$N_{H_2} \geq \frac{N_{HF}}{10} \approx 10^{15} \text{ cm}^{-3}$$

We shall now consider the preparation of an active mixture. It is formed by mixing a partly dissociated substance containing fluorine with a substance which contains hydrogen. The mixing time should be less than or of the order of the reaction time because otherwise the process of deactivation of the vibrationally excited HF molecules by collisions with fluorine radicals can significantly reduce the density of the active molecules. In accordance with the conditions (20) and (22), this requirement means that the mixing time  $\tau_m$  under optimal operating conditions should be several times shorter than  $10^{-5}$  sec. This condition can be satisfied by turbulent mixing in an effective mixing layer of thickness  $h$ , which is selected to satisfy

$$h \leq c_s \tau_m \quad (23)$$

( $c_s$  is the characteristic velocity of turbulent motion close to the velocity of sound) and which does not exceed a few tenths of a centimeter. We must bear in mind that in the case of turbulent mixing one also needs supersonic gas circulation.

The cw chemical HF laser system described above has been implemented in practice in many forms<sup>140-152</sup> differing in the nature of the substance containing fluorine, nozzle and resonator geometries, method used to form fluorine radicals, and power used to initiate the laser. Such major parameters as the specific output energy (270 J/g), chemical efficiency (up to 30%), and electrical efficiency ( $\geq 4\%$ ) make this laser one of the leaders. Moreover, there are no reasons in principle

why the output power of this laser could not be increased by increasing the dimensions of the system and the rate of supply of the working mixture and still keep the above characteristics and laser efficiency.

Estimates indicate that the practical chemical efficiency of such lasers is close to its theoretical value. The electrical efficiency is governed by the energy required to form a fluorine atom and it depends largely on the nature of the substance containing fluorine. We can expect the use of fluorine-containing substances with a lower binding energy of fluorine atoms than in SF<sub>6</sub> to increase correspondingly the electrical efficiency of such lasers. Some suitable substances are listed in Table XI.

We shall now consider the problems encountered in the use of weakly bound fluorine compounds in a laser operating as described above. A significant degree of dissociation of such molecules is attained at temperatures much lower than those in the system described above (the equilibrium degree of dissociation of the F<sub>2</sub> molecules is listed in Table V). However, the density of the fluorine radicals at the entry to a nozzle is limited by the possibility of their recombination



before the gas passes through the nozzle and becomes mixed with the substance containing hydrogen. This restriction can be represented in the form

$$(N_F^0 N_M k_{rec})^{-1} > \tau_c + \tau_m, \quad (25)$$

where  $k_{rec} \sim 10^{-33}$  cm<sup>6</sup>/sec is the rate constant of the process (24) and  $\tau_c$  is the typical time that the fluorine radicals spend in the reservoir in front of the nozzle. (Directional velocity of the gas in this reservoir is considerably less than the velocity of sound so that the minimum value of  $\tau_c$  cannot be less than 10<sup>-4</sup> sec.) As pointed out above, turbulent mixing of the components can make the mixing time  $\tau_m$  less than 10<sup>-4</sup> sec. The optimal density of a buffer gas  $N_M$  is several times higher than the density of fluorine radicals because only then the presence of a buffer diluent has the desired effect of increasing the specific heat of the mixture and the velocity of sound. If we assume that  $N_M \approx 10N_F$ , we find that the condition (25) gives

$$N_F^0 < 10^{18} \text{ cm}^{-3}, \quad (26)$$

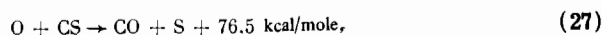
where the zero superscript denotes the state of the gas in front of the nozzle. If we assume that under optimal conditions each fluorine atom should react chemically to form a HF molecule, we find that the above restriction agrees with the condition (20) that limits the optimal value of the density of the HF molecules in the resonator.

TABLE XI. Average binding energy of fluorine atom in some compounds.

Molecule	F <sub>2</sub>	NeF <sub>6</sub>	SF <sub>6</sub>	NF <sub>3</sub>
Specific enthalpy, kcal/mole	18.5	29	76	64

## b) Carbon monoxide laser

In this type of laser a population inversion is formed as a result of a chemical reaction in a mixture of oxygen and carbon compounds. It is usual to employ CS<sub>2</sub> and O<sub>2</sub> (air). Photochemical, electric-discharge, or thermal initiation of such a mixture produces a sequence of reactions some of whose characteristics are listed in Table II. However, we can see from this table that the reactions in question occur in several stages and each of them has not yet been investigated fully, but it has been established that the excitation of the laser is due to the reaction



characterized by high values of the rate constant and energy defect. A considerable part of this defect is evolved as the energy of the vibrational degrees of freedom of the CO molecule.

Various modifications of the chemical CO laser differ from one another by the initial composition of the mixture and by the method of initiation of the reaction (27). The most widely used are two cw methods differing from one another by the principle of preparation and replacement of the active medium. In the first method, lasing occurs in a freely burning CS<sub>2</sub>+O<sub>2</sub> flame. This method is very attractive because it represents the most direct conversion of chemical energy into light without any energy supply devices.

The main factor which limits the output parameters of a CO laser excited by a freely burning flame is the heating of the active medium. In fact, since the oxidation of CS<sub>2</sub> requires about 200 kcal/mole, which heats the active medium to ~1000–2000°K, a population inversion in a circulating mixture occurs only in a narrow layer where practically all the energy is concentrated in the vibrational degrees of freedom of the reaction products. The thickness of this layer  $l$  can be expressed in terms of the mixture circulation velocity  $w$  and the characteristic VT relaxation time of the vibrationally excited CO molecules:

$$l \propto w \tau_{VT}. \quad (28)$$

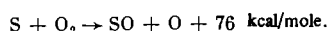
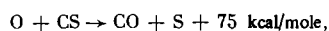
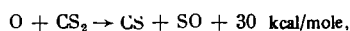
In practical systems (see, for example, Ref. 153), even at the maximum circulation velocities  $w \sim 10^4$ – $10^5$  cm/sec attained so far, the value of  $l$  is very small ( $\leq 0.1$  cm), which makes it difficult to achieve even partial extraction of the optical energy from the system. Consequently, the chemical efficiency of such a laser estimated for the reaction (27) does not exceed 1%. A more energy-efficient method is that involving excitation of a cw chemical CO laser in which the radicals needed for the CS<sub>2</sub>+O<sub>2</sub> chemical reaction are created by an electric discharge. This is usually achieved by circulating molecular oxygen through the discharge region. At the exit from the discharge region the oxygen is partly dissociated and it is directed back to the resonator where it is mixed with CS<sub>2</sub>. An important advantage of systems of this kind is the fact that in a wide range of the discharge parameters a

considerable proportion (80–90%) of the power supplied to the discharge in molecular gases is used to excite molecular vibrations and to dissociate molecules. This makes it possible to initiate reactions which excite a laser at the expense of relatively small energy losses.

Other important advantages of this excitation method of a cw chemical CO laser, compared with those discussed above, are related to the possibility of considerably lowering the temperature of the active medium in the reaction zone. Such lowering is ensured, on the one hand, by the high degree of dilution of oxygen with an inert gas and, on the other, by the use of a high velocity of circulation of the active medium through the resonator.

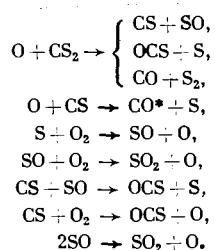
Electric-discharge excitation of a chemical CO laser may involve longitudinal (see, for example, Ref. 154) or transverse (see, for example, Ref. 155) discharges. The specific output energy (~65 J/g) and the chemical efficiency (~20%) are then comparable with the corresponding parameters of gas lasers of other types.

In estimating the potentialities of a chemical CO laser with electric-discharge initiation it is necessary to compare this laser with a cw CO laser excited directly in an electric discharge.<sup>156,157</sup> We must bear in mind that the efficiency of an electric discharge in the case of dissociation of molecular oxygen is 5–6 times power than in the case of excitation of vibrational states of the CO molecule by electron impact. Therefore, a cw chemical CO laser is competitive with an electric-discharge CO laser under the condition that for each oxygen atom formed in the discharge there are about ten vibrationally excited CO molecules. In other words, a chain reaction should be used for excitation. One of the possible chain reactions discussed in Ref. 154 involves the following elementary stages:

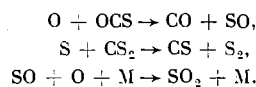


We can see that this reaction reduces the initial number of the oxygen atoms.

The mechanism of the  $\text{CS}_2 + \text{O}_2$  reaction with longer chains was suggested and investigated experimentally in Ref. 158, where the oxidation of  $\text{CS}_2$  was assumed to occur as follows:



We can see that a branched chain reaction with an increasing amount of atomic oxygen is possible in this system. This increase is limited by the processes



The length of the chain estimated in Ref. 158 is about 5 links. This ensures high output parameters of the laser with a specific output energy of ~170 J/g and a chemical efficiency of ~27%. Estimates indicate that in this case over twenty laser photons are emitted for each oxygen atom formed in the electric discharge. Such parameters, close to those of an electric-discharge CO laser,<sup>157</sup> are attainable only as a result of a chain reaction.

Even better parameters are reported for a chemical CO laser<sup>159</sup> in which the CS and S radicals required for the chain reaction between  $\text{CS}_2$  and  $\text{O}_2$  are formed as a result of burning of an  $\text{NF}_3\text{-CH}_4\text{-H}_2\text{-CS}_2$  mixture. Products of partial combustion of the mixture containing radicals of this type are mixed at the exit from a nozzle with dry air and with  $\text{N}_2\text{O}$ , which produces a stream of vibrationally excited CO molecules. The output power of such a system can reach 450 W in the cw regime. An important feature of such lasers is the absence of any external energy sources.

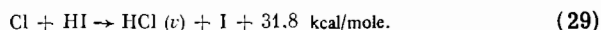
The energy characteristics of chemical CO lasers are comparable with those of the more widely used HF lasers. The relatively lower popularity of the former may be due to the existence of an electric-discharge CO laser which emits approximately the same lines and has similar specific output energy but is more convenient in the practical sense. The main attractive feature of a chemical CO laser is its use as means for investigating very complex chemical processes occurring in the oxidation of  $\text{CS}_2$ .

### c) Other types of cw chemical laser

The above cw HF, DF, and CO lasers have very high output parameters and are already used widely in research and technology. Lasers utilizing transitions in other diatomic or triatomic molecules are used less widely this being due to their poorer characteristics and also to the higher cost of the systems and reagents. A detailed analysis of those systems whose practical usefulness is not clear is outside the scope of our review. Nevertheless, we can briefly consider two systems whose potentialities are frequently discussed in the literature.

The first of these systems is a laser employing transitions in the HCl molecule, whose chemical and physical properties are closest to HF and can therefore be regarded as appropriate for a potential active medium of an efficient chemical laser. The simplest of the reactions producing vibrationally excited HCl

molecules is the substitution reaction, such as

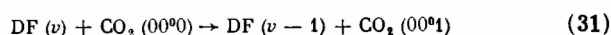


This reaction has been used to obtain cw lasing<sup>160</sup> by mixing of reagents at the exit from a supersonic nozzle. The Cl radicals needed for the (29) reaction are formed as a result of the reaction



which occurs in front of the nozzle. The output power of this laser, which does not require an external energy source (apart from the energy needed to compress the active medium before it enters the nozzle), is ~35 W. About 4.5% of the energy evolved as a result of the reaction (29) is transformed into the energy of laser radiation.

Another cw chemical laser characterized by fairly high output parameters operates on the basis of transfer of the vibrational energy from the DF to the CO<sub>2</sub> molecule:



followed by stimulated emission as a result of vibrational-rotational transitions in the CO<sub>2</sub> molecule.<sup>6</sup> The rate constant of the above excitation transfer process is fairly high (~5 × 10<sup>-13</sup> cm<sup>3</sup>/sec at T = 300°K) so that a suitable selection of the optimal composition of the mixture in this type of laser may ensure a fairly complete utilization of the vibrational energy evolved as a result of the reaction of fluorine with deuterium.

The transfer of the vibrational excitation from the DF to the CO<sub>2</sub> molecules is advantageous for two reasons. Firstly, the rate constant of the vibrational relaxation of the CO<sub>2</sub> molecules (~10<sup>-14</sup> cm<sup>3</sup>/sec) is considerably lower than the corresponding constant of the DF molecules and this eliminates the undesirable influence of the relaxation process on the output parameters of the laser and makes it possible to operate at much higher pressures in the active medium. Moreover, the addition of CO<sub>2</sub> which acquires a considerable part of the vibrational energy evolved in the system extends considerably the range of pressures in which the D<sub>2</sub>:F<sub>2</sub> mixture remains chemically stable.

The main factor which inhibits extensive practical use of this system of excitation of a CO<sub>2</sub> laser is the relatively high cost of deuterium compounds, which are then used to generate coherent λ ≈ 10.6 μ radiation that can easily be generated by other (nonchemical) methods. Nevertheless, the number of experimental and theoretical investigations of this laser is fairly high and in many of them<sup>161-166</sup> it has been reported that units with high output parameters and quite convenient in practical use have been constructed. Distinguishing features of these units are the use of purely chemical initiation of the reaction, so that the fluorine radicals necessary for the reaction are produced by the spontaneous process



## 6. PULSED CHEMICAL LASERS

The output power of chemical lasers can be increased, as in the case of lasers of other types, by increasing the pressure of the active substance in the resonator. In the cw case the maximum pressure is limited by Eq. (20) and even when supersonic gas circulation is used, this pressure cannot exceed a few Torr. Pulsed operation is necessary in order to increase the pressure of the active medium and, consequently, the output characteristics of chemical lasers. An increase in the gas pressure increases the rates of all the bulk processes and the effective utilization of the vibrational energy of the molecules formed as a result of a chemical reaction is possible if the duration of the stimulated emission pulses does not exceed the characteristic vibrational relaxation time of the colliding molecules. If we bear in mind that the time necessary for the development of stimulated emission in a large system is 10<sup>-8</sup>-10<sup>-7</sup> sec, we can see that the use of the pulsed regime can increase the output parameters of a chemical laser by 2-3 orders of magnitude. We shall now consider the specific features of the operation of lasers in the pulsed regime and the optimal conditions in this regime.

### a) Chain reaction lasers

This is the most interesting type of chemical laser which, after the first experiments<sup>119</sup> in the Soviet Union, has attracted close attention of laser scientists and engineers. This interest is explained by the extremely high energy characteristics: the output energy of such a laser can be approximately an order of magnitude higher than the energy lost in the initiation process.<sup>5)</sup> The active medium in lasers utilizing the chain reaction of burning fluorine in hydrogen usually consists of a mixture of F<sub>2</sub>, H<sub>2</sub>, and a buffer gas (He or Ar) which increases the specific heat of the mixture. Sometimes the mixture is supplemented by a small amount of polyatomic molecules containing fluorine and/or hydrogen (for example, SF<sub>6</sub> and CH<sub>4</sub>) which reduce somewhat the chain reaction rate. A small amount of oxygen, which prevents spontaneous combustion of the mixture at a high pressure and makes it easier to store it, is added for the same purpose.

Initiation of the chemical reaction resulting in the excitation of such a laser can be by a pulsed discharge or by irradiation with ultraviolet or ionizing radiation. Since the chain reaction of fluorine with hydrogen requires simply a small number of free fluorine atoms, we can expect the output energy of this laser to be many

<sup>5)</sup> Here and later, we shall describe the efficiency of excitation of pulsed chemical lasers by the ratio of the laser radiation energy obtained from a given volume of the active medium to the energy deposited in this volume. The definition makes it possible leaving out of consideration the influence of specific features of any given system to characterize the physical method of initiation of a chemical laser.

times greater than the energy lost in the initiation process. However, in the case of a low initial degree of dissociation of the molecular fluorine the chain reaction is accompanied by a rapid accumulation of HF molecules which increase the rate of vibrational relaxation of the active molecules. Therefore, at some moment of the reaction, which depends on the initial degree of dissociation of the  $F_2$  molecules, the rate of formation of the vibrationally excited HF molecules by the chain reaction is lower than the rate of collisional deactivation of the same molecules. Thus, the lifetime of a population inversion is found to be shorter than the duration of the whole reaction between fluorine and hydrogen, so that the chemical energy stored in the active medium is utilized only very partially.

We shall now analyze the relationship between the initial degree of dissociation of dissociation of the molecular fluorine and the utilization coefficients  $\eta_e$ , of the energy lost in the initiation, and  $\eta_c$  of the chemical energy stored in the active medium.<sup>7,167</sup> With this in mind we shall consider a simple model according to which a simple chain reaction (13), (14), producing vibrationally excited HF\* molecules occurs in a stoichiometric  $H_2 + F_2$  mixture with an initially low degree of dissociation of the molecular fluorine  $\varepsilon = [F]_0/[F_2]_0 \ll 1$ . If the HF molecule is modeled by a two-level system, the rate equation for the density of the vibrationally excited molecules  $N_{exc}$  is<sup>167</sup>

$$\frac{dN_{exc}}{dt} = k_1 N_F N_{H_2} + k_2 N_H N_{F_2} - N_{exc} N_{HF} k_{VT}, \quad (33)$$

where  $k_1$  and  $k_2$  are the rate constants of the reactions (13) and (14);  $k_{VT}$  is the rate constant of the vibrational relaxation of the HF molecules when they collide with one another. (We are assuming that this constant is independent of the degree of vibrational excitation of the quenching molecules.) We can easily show that during the initial stage of the reaction the concentration of the HF molecules rises linearly with time  $N_{HF} = A\varepsilon t$  ( $A$  is the coefficient of proportionality), whereas the first two terms on the right-hand side of Eq. (33) are practically constant. Hence, we find that the density of the excited molecules assumes its maximum value at the moment  $t_i \propto \sqrt{1/\varepsilon}$  and then this density decreases rapidly to well below the total density of the HF molecules. The time  $\tau_i$  can be regarded as the lifetime of a population inversion in the system. However, the total reaction time is  $\tau_r$  which is obviously proportional to  $\varepsilon^{-1}$ . Thus, if the initial degree of dissociation of the molecular fluorine is low, only a small proportion of the evolved chemical energy proportional to the value of  $\sqrt{\varepsilon}$  is utilized. On the other hand, the ratio of the laser radiation energy to the energy lost in the initiation of the reaction (the latter is clearly proportional to  $\varepsilon$ ) is proportional to  $\varepsilon^{-1/2}$  and at low values of  $\varepsilon$  this quantity (known as the electrical efficiency of a laser) may exceed unity.

We can thus see that the values of the electrical and chemical efficiency of a laser excited by a chain reaction are inversely proportional to one another: a reduction in the initiation energy of a laser and a corre-

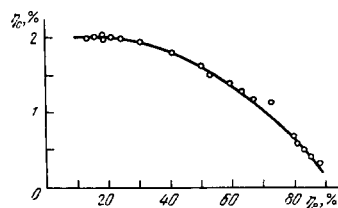


FIG. 10. Relationship between the electrical  $\eta_e$  and chemical  $\eta_c$  efficiencies of a laser excited by a chain reaction between fluorine and hydrogen<sup>169</sup> in a mixture with the following partial pressures:  $p_{H_2} = 3$  Torr,  $p_{F_2} = 3$  Torr,  $p_{O_2} = 0.75$  Torr,  $p_{He} = 30$  Torr.

sponding increase in  $\eta_e$  results in a simultaneous reduction of the degree of utilization of the chemical energy released as the result of the reaction.

These conclusions, deduced by us on the basis of a rough model, are supported by the results<sup>167</sup> of consistent calculations of the dynamics of amplification in a pulsed HF laser excited by a chain reaction.<sup>6)</sup> Another reason for incomplete utilization of the chemical energy evolved as a result of the chain reaction between fluorine and hydrogen is the heating of the active medium by the exothermal reaction and resultant quenching of the population inversion in the system well before the end of the reaction. The role of this effect discussed in Ref. 168 can be reduced by diluting the active medium with an inert gas or with a polyatomic gas containing fluorine (for example,  $SF_6$ ), which increases the specific heat of the active medium and thus reduces the heating.

The reduction in the chemical efficiency of a laser excited by a chain reaction on increase in its electrical efficiency discussed above is supported by an experimental investigation<sup>169</sup> whose results are plotted in Fig. 10. This investigation was carried out on a small ( $1 \times 0.8 \times 15$  cm) laser system excited by a transverse electric discharge supplied with pulses of 0.01–0.25 J energy and 0.2–0.7  $\mu$ sec duration. An  $F_2:H_2:He:O_2$  mixture with a 1:1:1:10:0.6 composition and a total pressure of up to 120 Torr was circulated through the laser chamber at a velocity of 8 m/sec. The relationship between  $\eta_e$  and  $\eta_c$  was more complex than that given by the simple model estimates obtained above. For example, at low values of the electrical efficiency  $\eta_e \leq 10\%$ , corresponding to the initial degree of dissociation of the molecular fluorine close to unity, the value of  $\eta_c$  remains practically constant. This means that,

<sup>6)</sup> The influence of VT relaxation of the active molecules on the chemical efficiency of a pulsed HF laser was also investigated earlier,<sup>6,9</sup> but since at that time there were no data on the VT relaxation, the results were not in agreement with the experiments reported in Ref. 169.



irrespective of the value of  $\epsilon$ , the time for the development of a chain reaction is so short that the process of VT relaxation does not have time to affect the nature of lasing. The range  $40 \leq \eta_e \leq 80\%$  is described quite well by the dependence  $\eta_e \propto \eta^{-1}$ . The range where  $\eta_e \sim 1$  corresponds to small values of  $\epsilon \sim 0.01$ . A steeper reduction in the utilization coefficient of the chemical energy observed in this range on increase in  $\eta_e$  is clearly due to the circumstance that stimulated emission now occurs under near-threshold conditions.

The number of laser systems whose electrical efficiency is greater or of the order of unity is fairly large.<sup>168-181</sup> Selected parameters of such systems are listed in Table XII. It follows from the penultimate column of this table that only a small fraction of the HF molecules formed by the reaction contributes to lasing. This confirms the above conclusion of partial utilization of the vibrational energy when the initial degree of dissociation of the molecular fluorine is low.

### b) Pulsed lasers using simple substitutional reactions

Pulsed chemical lasers utilizing simple substitutional reactions and usually excited by a transverse electric discharge are much more convenient in practical applications. Lasers of this type are characterized by relatively low output parameters (energy per pulse a fraction of a joule and the electrical and chemical efficiencies not exceeding a few percent), but the simplicity, explosion-proof operation, and low cost, together with the chemical stability of the active medium permitting operation at a high repetition frequency, have made these lasers popular.

TABLE XII. Parameters of pulsed chemical lasers with high electrical efficiency excited in F<sub>2</sub> + H<sub>2</sub> chain reaction by various methods (I—electron beam, II—transverse discharge, III—discharge with preionization, IV—ultraviolet radiation).

Excitation method	Partial pressures of active mixture, Torr	Active volume, liter	Pulse duration, $\mu$ sec	Excitation energy, J	Output energy, J	Specific output energy		$\eta_e, \%$	$\eta_c, \%$	Quantum yield, photons/molecule	Ref.
						J/l	J/g				
II	F <sub>2</sub> (18), H <sub>2</sub> (4), O <sub>2</sub> (1.5), He (215)	—	—	0.104	0.115	—	—	—	—	—	170
II	F <sub>2</sub> (10), H <sub>2</sub> (10), O <sub>2</sub> (0.6), He (100)	0.012	1.5	0.01	0.01	—	—	—	—	—	169
I	F <sub>2</sub> (360), O <sub>2</sub> (140), H <sub>2</sub> (100), SF <sub>6</sub> (100)	24.5	0.06	1300	2340	95.5	43.4	180	3.3	0.2	171
III	F <sub>2</sub> (48), H <sub>2</sub> (24), Ar (300), He (430)	0.06	1.5	1.45	2.52	42	46	148	6.3	0.3	177
I	F <sub>2</sub> (120), H <sub>2</sub> (120), SF <sub>6</sub> (180)	0.23	0.5	900	11	48	29	1.2	1.7	0.08	173
I	F <sub>2</sub> (72), H <sub>2</sub> (72), SF <sub>6</sub> (96)	4.2	0.5	900	50	12	13.5	5.6	0.63	0.03	173
I	F <sub>2</sub> (800), O <sub>2</sub> (240), H <sub>2</sub> (200), SF <sub>6</sub> (100)	32.3	0.02	7000	4200	130	42.2	180	2.1	0.13	179
IV	F <sub>2</sub> (140), O <sub>2</sub> (70), H <sub>2</sub> (42)	4.5	5	1300	40	8.9	20	0.03	0.67	0.044	188
I	F <sub>2</sub> (230), O <sub>2</sub> (8), H <sub>2</sub> (60), He (460)	0.104	2	140	5.1	51	97	875	2.8	0.17	180
I	F <sub>2</sub> (275), H <sub>2</sub> (95), O <sub>2</sub> (20), He (790)	0.12	0.4	7	12	100	125	900	4	0.23	181
IV	F <sub>2</sub> (76), H <sub>2</sub> (9), O <sub>2</sub> (5), Ar (670)	12.8	—	1000	292	25	13	30	8.1	0.4	176

The active medium in lasers of this type usually consists of a mixture of a substance containing fluorine (for example, SF<sub>6</sub>) and hydrogen or a substance containing hydrogen (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, etc.), which is usually diluted by an inert gas (He, Ar) in order to improve the discharge properties. The laser is excited by a pulsed transverse discharge using methods developed in the last decade and thoroughly tested as means of pumping high-pressure molecular lasers. The auxiliary equipment includes a unit generating short high-voltage pulses, electrodes of special configuration ensuring a uniform breakdown of the discharge gap, and sometimes also additional electrodes used to strike an auxiliary discharge, which facilitates a uniform initiation of the main discharge. This technique makes it possible to use relatively simple and inexpensive systems of producing a uniformly distributed pulsed discharge in a high-pressure (atmospheric) gas when the electrode separations are of the order of 1 cm or greater. Circulation of the active medium at right-angles to the electric field and to the optic axis permits continuous cooling and replacement of the working mixture and, consequently, makes it possible to construct systems with a high repetition frequency.

The number of papers on the development and investigations of transversely excited pulsed chemical lasers is very large (over 100). The most interesting among recent studies are those reported in Refs. 182–194 and summarized in Table XIII. We can see, by comparison of Tables XII and XIII, that the specific output characteristics of lasers of this type are on the average about an order of magnitude poorer than the corresponding characteristics of lasers excited by chain reactions. This easily explainable observation is due to the fact, that for any of the types of laser discussed above, the

TABLE XIII. Parameters of pulsed chemical lasers excited by direct substitution reactions using various methods (I—transverse discharge, II—discharge with photoinitiation, III—discharge with electron initiation)

Partial pressures in active mixture, Torr	Excitation method	Active volume, liter	Output pulse duration, nsec	Excitation energy, J	Output energy, J	$\eta_e, \%$	Quantum yield, photons/molecule	Specific output energy		Repetition frequency, Hz	Ref.
								J/l	J/g		
He (750), SF <sub>6</sub> (12), C <sub>2</sub> H <sub>6</sub> (1)	II	0.24	16	28	0.425	1.5	—	—	—	—	182
SF <sub>6</sub> (10), H <sub>2</sub> (4)	I	0.069	220	0.08	3.5 · 10 <sup>-4</sup>	0.45	—	—	—	—	183
To He	I	0.069	220	0.08	10 <sup>-4</sup>	0.01	—	—	—	—	183
SF <sub>6</sub> (50), H <sub>2</sub> (4)	I	0.69	190	56	0.6	1	—	—	—	—	184
SF <sub>6</sub> (70), Ar (30), H <sub>2</sub> (5)	III	0.2	50	4.7	0.14	3	—	—	—	—	184
SF <sub>6</sub> (20), C <sub>2</sub> H <sub>6</sub> (0.4)	I	0.07	—	1.9	0.03	1.6	—	—	—	—	185
SF <sub>6</sub> (250), H <sub>2</sub> (20), He (280)	I	0.06	60	25	1	4	—	—	—	—	186
SF <sub>6</sub> (50), H <sub>2</sub> (17)	I	0.29	170	3000	1.8	0.06	—	—	—	—	187
SF <sub>6</sub> (105), H <sub>2</sub> (15)	I	0.2	300	40	0.9	2.3	—	—	—	—	188
SF <sub>6</sub> (30), H <sub>2</sub> (5)	I	0.1	1000	0.2	0.0025	1.2	—	—	—	—	189

energy required to form one fluorine atom depends weakly on the initiation method and is usually 10–20 times greater than the energy of a laser photon. This ratio of the energies governs the maximum efficiency of lasers of the type under discussion, which does not exceed a few percent. On the other hand, the efficiency of the chain-reaction lasers exceeds this value by a factor equal to the number of links in the chain that can take place before a population inversion disappears. In spite of the lower values of the efficiency and specific output energy, the lasers excited by a transverse discharge are employed extensively in laboratory studies.

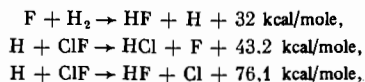
### c) Other types of pulsed chemical lasers

Although the main trend in the research and development of chemical lasers has been to concentrate on the HF and DF molecules, there are many other molecules which can be used to convert chemical energy into light. For example, fairly high output parameters are typical of pulsed lasers utilizing transitions in the HBr molecule formed as a result of the reaction



This laser can be easily excited by longitudinal<sup>195</sup> and transverse<sup>196–201</sup> discharges, and (in the most successful systems) the values of the efficiency and pulse energy are of the same order of magnitude as in the case of the HF (DF) lasers discussed above.

Another interesting type of chemical laser utilizes transitions in the HCl molecule and is excited by the reaction (29). Judging by the published information,<sup>202–212</sup> the specific output parameters of this laser are an order of magnitude poorer than the corresponding parameters of the HF laser. The maximum energy of the laser radiation pulses does not exceed 20–30 mJ (Ref. 207) if the reaction is photoinitiated and the laser efficiency is 10<sup>–20</sup>%. It follows from experimental studies<sup>208, 209</sup> that the low output characteristics of the hydrogen chloride laser are due to the undesirable effects of processes which destroy the vibrational excitation of HCl molecules as a result of collisions with Cl atoms and with HCl and Cl<sub>2</sub> molecules. It has recently been reported<sup>212</sup> that a considerable increase in the output characteristics of this laser can be achieved by using the compound ClF. Mixing of this compound with hydrogen produces a chain reaction



which results in a population inversion of the transitions in the HF and HCl molecules simultaneously.

It must be generally stressed that the appearance of a population inversion of vibrational-rotational transitions in diatomic molecules formed as a result of sufficiently fast exothermal reactions is a rule rather than the exception. For example, Table XIV lists the parameters of lasers described in Ref. 213 and utilizing pulsed oxidation of various elements. These ele-

TABLE XIV. Parameters of pulsed lasers excited by oxidation of elements forming exploding wires.

Element	Oxidizer	Oxidizer pressure, Torr	Duration of output pulses, $\mu\text{sec}$	Range of emission wavelengths, $\mu$	Energy of zeroth vibrational quantum, $\text{cm}^{-1}$	Heat of reaction, kcal/mole
Li	F <sub>2</sub>	25.6	2.6	16–13	914.33	101.0
C	F <sub>2</sub>	41.0	2.0	24–10.5	1308.1	91.0
C	O <sub>2</sub>	71.8	2.0	24–5	2169.52	137.8
Mg	F <sub>2</sub>	28.2	1.5	13.5–12.8	717.6	69.5
Mg	F <sub>2</sub>	30.1	2.8	14–12.8	717.8	69.5
Al	F <sub>2</sub>	24.6	1.7	13.5–12.5	804.95	122.5
Ti	F <sub>2</sub>	24.8	1.6	24–11.1	593.0	110.1
Ti	NF <sub>3</sub>	26.2	1.7	24–5	593.0	87.5
Ti	O <sub>2</sub>	65.5	1.4	24–10.5	1008.4	49.7
Fe	F <sub>2</sub>	28.4	2.2	24–11.1	630.0	69.2
Ni	F <sub>2</sub>	25.8	2.2	24–10.5	740.0	66.0
Cu	F <sub>2</sub>	26.7	2.1	24–11.1	621.89	50.1
Pt	F <sub>2</sub>	28.1	2.4	24–11.4	—	—
Au	F <sub>2</sub>	28.6	1.3	24–10.5	—	35.0
U	F <sub>2</sub>	30.5	3.0	24–10.5	483.0	126.0
U	O <sub>2</sub>	51.7	1.9	16–8.8	920.0	60.2

ments are components of thin wires which are exploded electrically in an oxidizing atmosphere, which results in rapid oxidation of the elements and formation of vibrationally excited diatomic molecules. We can see that the range of the stimulated emission wavelengths of such pulsed lasers covers a considerable part of the infrared spectrum.

## 7. CONCLUSIONS

Investigations and the development of chemical lasers have tackled the problem of conversion of chemical energy into the energy of coherent radiation. However, the importance of these investigations go well beyond this problem. From the scientific point of view, a chemical laser is a system where in a relatively small volume a rich variety of chemical, relaxational, gas-dynamic, and other processes takes place. The nature of these processes and their mutual influence determine the parameters of a chemical laser. Therefore, investigations of chemical lasers stimulated primarily by their applications provide a unique opportunity for studies of the processes occurring in nonequilibrium chemically active molecular gases subjected to the action of external energy sources. The branch of science concerned with such topics is now growing rapidly; this can also be seen from our review. We thus have one more example of a strong reaction of applied research on fundamental science.

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