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A new class of chemical lasers based on electronic transitions of atoms, radicals, or molecules excited via oxidation chain reactions in the presence of catalysts is proposed and discussed. The possibility is considered of using these processes to realize four lasing schemes: directly via transitions of excited intermediate products, in an exchange chemical laser, using narrowband "chemical lamps," and in chemical-excimer lasers. A number of specific active mixtures are proposed. The gain of a realizable chemical Na-BaO laser is calculated. The possibility of using chemical reactions with participation of cluster molecules are analyzed. The use of atoms as acceptor (emitting) particles is discussed. Two methods of obtaining increased atom densities are proposed. Certain possibilities of obtaining cw lasing on self-limiting atom transitions are considered.

#### 1. INTRODUCTION

The most widely used at present are chemical HF and  $DF-CO_2$  lasers emitting on vibrational-rotational transition of the lower electronic state of the working molecules in the IR spectrum [1-3]. Their operation is based on a chain mechanism of exciting the molecules that are the products of hydrogen fluorination. In the first of these lasers the emitting molecules are HF (2.5-3.4  $\mu$ m), and in the second CO<sub>2</sub> (10.6  $\mu$ m), which does not participate directly in the reaction but obtains energy from the vibrationally excited products (DF molecules) in a quasiresonant v-v exchange process.

A significant recent achievement is the development and perfection of a purely chemical oxygen-iodine  $(O_2-I)$  laser that emits on the electronic magnetodipole transitions  $5^2P_{1/2} \rightarrow 5^2P_{3/2}$  ( $\lambda = 1.315 \ \mu m$ ) of atomic iodine. Its operation is based on quasiresonant electron-electron (E-E) energy transfer from chemcially produced oxygen molecules  $O_2(a^1\Delta)$ to iodine atoms  $I(^2P_{3/2})$ . Population inversion in a chemical  $O_2$ -I laser was first recorded by the authors of [4], and lasing was first reported in [5].

The principle of electron-electron energy exchange in chemical lasers can be extended to include a number of other atoms. In particular, great interest attaches to the use of acceptor (emitting) molecules constituting halogens and interhalogens in conjunction with metastable donor molecules (or radicals) produced in fast chemical reactions [6, 7]. The possibility of using halogens and interhalogens in chemical lasers was reported at the second international conference on "Trends in Quantum Electronics" (Bucharest, 1985). Interest in such lasers is due to the feasibility, in principle, of developing high-power coherent sources for the IR and visible bands.

A number of questions connected with chemical operation of electronically excited donor molecules, radicals, and atoms, as well as with the choice of appropriate donor-acceptor pairs, are considered in [6-12].

We propose and consider here a new class of chemical lasers on electronic transitions of atoms or molecules excited by oxidation chain reactions in the presence of a catalyst. The basic difference between these reactions and the well-investigated hydrogen-fluorination chain reaction  $H_2 + F_2$  is that the intermediate (and not final) products are in excited

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states [8-11]. We analyze here a number of additional questions connected with the feasibility of developing chemical lasers on electronic transitions (the chemical-excimer mechanism, exchange lasers, use of atoms as emitting particles, new kinetic systems, use of cluster molecules in reactions, and others).

# 2. OXIDATION CHAIN REACTIONS WITH A CATALYST

The initial mixture of a possible chemical laser on electronic transitions consists of a fuel (F), oxidant (PO), and a catalyst (K). The general scheme of the chain oxidation of the electronic states can be represented in the form

$$K(K^*) + PO \xrightarrow{K_1} KO(KO^*) + P + E_1(E_1^*)$$
(1)

$$KO(KO^*) + F \xrightarrow{K_2} K^*(K) + FO + E_2(E_2^*)$$
 (2)

$$PO + F \xrightarrow{k_3} P + FO + E_3, \qquad (3)$$

where K is the catalyst atom, F the fuel, PO the oxidant, O an atom of the main subgroup of the sixth (O, S, Se, Te) and seventh (F, Cl, Br, I) groups of the periodic table (or a radical), P and FO are the final products of the chain process, an asterisk labels the corresponding electronically excited state,  $E_1(E_1^*)$ ,  $E_2(E_2^*)$  and  $E_3$  are the energies released. Note that in the absence of fuel only the first link (1) of the chain (1)-(3) remains, and its end product is the oxide KO.

Combustion of the initial components (F and PO) in the course of the chain process (1)-(3) results in products (P and FO), while the catalyst atom K and its oxide KO assume the role of active centers.

It is possible in principle to consider here four methods of utilizing the chain excitation product (1)-(2):

1. Obtaining direct lasing on the transitions of the intermediate products (the atoms of the catalyst K or its oxides KO).

2. Lasing on electronic transitions of the acceptor A excited in the quasiresonant exchange process

$$D^* + A \xrightarrow{k_4} D + A^* (D = K \text{ or } K\Theta).$$
(4)

3. Production of a selective chemical lamp for optical pumping of solid, liquid, and gaseous media by the narrow-band spontaneous radiation of the excited atoms of the catalyst  $(K^*)$  or of its oxide  $(KO^*)$ .

4. Production of chemical-excimer lasers based on the recombination process

$$K^{*}(KO^{*}) + X + Y \xrightarrow{k_{5}} KX^{*}(KOX^{*}) + Y$$
(5.1)

followed by the process

$$KX^*(KOX^*) \longrightarrow K(KO) + X + h\nu$$
(5.2)

where X is a noble-gas atom. Note that the loss of active centers in the process (5.1) and their recovery in (5.2) do not influence the production of the initial products F and PO.

From among the large number of chemical processes (1-3) we are interested in those in which the links (1) and (2) predominate and are accompanied by formation of K\* and (or) KO\*. This condition imposes definite requirements on the constants of the elementary acts and on the properties of the reagents, and makes it possible to narrow down the range of initial substances and choose the most promising among them. Let us formulate these requirements:

1. To avoid unprofitable production of initial amounts of oxidant and fuel it is necessary that the rate of the chain process (1)-(2) exceed substantially the rate of the direct reaction (3), i.e.,  $k_1$ ,  $k_2 >> k_3$ .

2. The condition connected with the formation of the electronically excited intermediate products K\* and KO\* calls for satisfaction of the Wigner-Witmer rule (spin conservation).

3. To produce an electronically excited catalyst atom KO\* it is necessary that the following condition be met by the bond energies E(K-O) of the catalyst-oxide, E(P-O) of the initial oxidant, and  $E(KO^*)$  of the catalyst-oxide excitation:

$$E(KO^*) \leq E(K \cdot O) - E(P \cdot O) \tag{6}$$

4. For an electronically excited catalyst atom K\* to be produced, the following condition must be met by the binding energies E(K-O) of the catalyst oxide, E(F-O) of the product, and  $E(K^*)$  of the catalyst atom:

$$E(K^*) \le E(F-0) - E(K-0).$$
 (7)

## 3. CHOICE OF REAGENTS FOR A CHAIN PROCESS WITH A CATALYST

The requirements formulated above permit a task-oriented search for the initial reagents.

It follows from condition (6) that the oxidant binding energies E(P-O) must be low enough. A number of prospective oxidants are listed in Table 1, which indicates the ground state of the oxidant PO, the binding energy, and the ground state of the reaction product P. Our aim was to obtain oxidant molecules with binding energy E(P-O) in the range 0.5-3 eV.

In the search for fuel, the aim was to obtain molecules with high dissociation energy  $D_0(F)$  and high binding energy E(F-O) of the fuel oxide. In this situation the binding energy of the fuel oxide determines the upper limit of the electronic excitation of the catalyst atoms. There are many known molecules and radicals with binding energy higher than 5 eV. These include:

a) compounds of d-elements of the 3rd (first subgroup - Sc, Y, lanthanides) with elements of the 6th group (O, S, Se, Te);

b) compounds of d-elements of the 4th period (Sc, Ti, V, Cr, Mn, Fe, Co, Ni) with elements of the 6th group;

c) various molecules and radicals, e.g., CO, SO, CS, CSe, CF,  $CF_2$ , CH,  $CH_2$ , etc.

Some promising possible fuels are listed in Table 2, in which are indicated the fuel molecules (ground state), their dissociation energy, and the ground state of the corresponding oxides and their binding energies.

# 4. CHOICE OF CATALYST FOR CHAIN PROCESS. POSSIBLE LASER TRANSITIONS

Taking into account the need for meeting the energy conditions (6) and (7) and the spinconservation conditions in each link of the chain process (1)-(2), and bearing in mind furthermore the spectroscopic data of Tables 1 and 2 and the characteristic values of the catalystoxide binding energies, we can conclude that most elements of the periodic table can serve as catalysts, with the exception of carbon, boron, inert gases, certain lanthanides, and tantalum (no radioactive elements are considered).

It should be noted that the constants  $k_1$  and  $k_2$  and the probability of formation of the electron-excited states K\* and KO\* depend on the reagent spin and on the chain-reaction products. From this viewpoint, catalysts can be arbitrarily divided into three groups:

I. Catalysts whose ground and lower electron-excited states have equal spins (elements of the lst, 3rd, and 7th groups of the periodic table).

II. Catalysts with different spins of the ground and lower electron-excited states (2nd and 5th groups).

III. Catalysts having different lower excited-state levels, with spin either equal or unequal to that of the ground state (4th and 6th group).

A similar subdivision of the oxides KO, while possible, is difficult because the electronic terms of many of them have not been reliably identified in the literature.

Oxidant P—O (ground state)	Oxidant binding energy E(P-O), eV	Product P (ground state)
CO3	0.5	$\operatorname{CO}_{2}(^{1}\Sigma)$
$O_3(\widetilde{X}^1A_1)$	1.11	$O_2(X^3\Sigma_g^-)$
$H_2O_2(\widetilde{X}^1A)$	1.49	$H_2O(\widetilde{X}^1A)$
$N_2 O(\widetilde{X}^1 \Sigma^+)$	I.69	$N_2(X^1\Sigma)$
NO <sub>3</sub> ( <sup>2</sup> A)	2.13	$NO_2(X^2A_1)$
$\operatorname{ClO}_2(\widetilde{X}^2B_1)$	2.5	СlO (Х <sup>2</sup> П)
СlO(X <sup>2</sup> П)	2.76	$Cl(^2P_{3/2})$
$NO_2(\widetilde{X}^2A_1)$	3.11	$NO(X^2\Pi_1)$
CH <sub>3</sub> NO <sub>2</sub>	< 2.6	CH <sub>3</sub> NO
C <sub>2</sub> H <sub>5</sub> NO <sub>3</sub>	< 2.6	C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>
C <sub>5</sub> H <sub>11</sub> ONO	< 2.6	C <sub>5</sub> H <sub>11</sub> ON

TABLE 1. Possible Candidates for the Role of Oxidant (PO)

We pay attention in the present paper only to catalysts of group I. In this case the Wigner-Witmer rule imposes no restrictions on the term of the catalyst produced in reaction (2); we can therefore hardly expect the excitation of K to be selective in this reaction. The same holds for the corresponding oxide KO [reaction (1)].

We note in this connection highly interesting studies [13-15] in which intense chemiluminescence was observed on the D lines of sodium (Na) atoms  $({}^{2}P_{1/2} \rightarrow {}^{2}S_{1/2}$  and  ${}^{2}P_{3/2} \rightarrow {}^{2}S_{1/2}$ transitions) in a CO + N<sub>2</sub>O + Na mixture; this is evidence of direct population of the first electron-excited levels  ${}^{2}P_{1/2}$  and  ${}^{2}P_{3/2}$  of sodium in the reaction (2). It is quite probable that this situation obtains also for other alkali metals.

Table 3 lists certain catalyst atoms and their limiting excitation levels for a number of fuels.

Of considerable interest are processes that are possible energywise and from the standpoint of the spin rule, for alkali metals having a low ionization potential

$$KO(^{2}\Pi) + F \rightarrow \begin{cases} K^{+}(^{1}S_{0}) + e + FO \\ K^{+}(^{1}S_{0}) + FO^{-} \end{cases}$$
(8)

These processes can, in principle, be of interest in connection with the feasibility of producing a low-temperature plasma by purely chemical means, and of producing a chemi-ionization laser. One cannot exclude the possibility that they play a role also in the formation of "ball lightning."

A distinctive feature of the alkali group of catalysts is that their oxides KO have low binding energy. Appreciable energy can therefore be released in the reaction (2) and part of it can excite electronic states of the catalyst atoms. One can hardly hope to develop chemical lasers on transitions to lower states, since the ground term of an alkali metal has the lowest statistical weight.

Fuel (F) (ground state)	(ground Dissociation energy Product F-0 ) $D_0(F)$ , eV (ground state)		Binding energy E(F-O) of pro- duct F-O, eV	
$CO(X^{1}\Sigma^{+})$	II.I	$CO_2(^1\Sigma)$	5.57	
$SO(X^3\Sigma^{-})$	5.37	$SO_2(\widetilde{X}^1A)$	5.75	
NdO	7.4	NdO <sub>2</sub>	6.2	
$TiO(X^3\Delta_i)$	6.9	$\operatorname{TiO}_{2}(\widetilde{X}^{1}A_{1})$	6.24	
$ScO(X^2\Sigma^+)$	6.95	$ScO_2(X^2A)$	6.42	
$VO(X^4\Sigma)$	. 6.42	$VO_2(\widetilde{X}^2A)$	6.49	
$YO(X^2\Sigma^+)$	7.4	$YO_2(\widetilde{X}^2A)$	6.8	
$CF(X^2II_{1/2})$	5.65	CFO	6.9	
$CeO(^{3}\Phi)$	<sup>3</sup> Φ) 8.2 CeO <sub>2</sub>		7.0	
$CS(X^{1}\Sigma^{+})$	7.29	$COS(^{1}\Sigma)$	7.05	
LaO $(X^2 \Sigma^+)$	$(X^{2}\Sigma^{+}) \qquad 8.25 \qquad LaO_{2}(\widetilde{X}^{2}A)$		7.35	
$CF_2(^1A)$	5.23 (CF·F) CF <sub>2</sub> O		7.4	
CH <sub>2</sub> ( <sup>3</sup> A)	4.45 (CH-H)	$H_2CO(^1A_1)$	7.9	
$CSe(^{1}\Sigma^{+})$	6.0	$\operatorname{COSe}(^{1}\Sigma)$	8.3	
СН(X <sup>2</sup> П)	3.46	HCO( <sup>2</sup> A)	8.4	

TABLE 2. Possible Candidates for the Role of Fuel (F)

For certain fuels, however, the excitation can extend to high-lying terms of the atoms, up to the ionization limit (alkali metals). This uncovers a possibility of obtaining lasing on transitions between excited states of atoms.

We cite some examples:

1. NaO(<sup>2</sup>I) + CSe(<sup>1</sup> $\Sigma$ )  $\rightarrow$  Na (up to ionization) + COSe(<sup>1</sup> $\Sigma$ ) + 5.69 eV: possible laser transitions are

$$\begin{cases} 10p({}^{2}P_{1/2}^{0}) \rightarrow 9d({}^{2}D_{5/2}^{}), \ \lambda = 100 \ \mu\text{m} \\ 8s({}^{2}S_{1/2}^{}) \rightarrow 3p({}^{2}P_{3/2}^{0}), \ \lambda = 0.45 \ \mu\text{m} \end{cases}$$
  
2.  $CsO({}^{2}\Sigma) + CO({}^{1}\Sigma) \rightarrow Cs^{*}(to 9p({}^{2}P_{3/2}^{0})) + CO_{2}({}^{1}\Sigma) + 3.43 \ \text{eV}: \text{ transitions are} \\ \begin{cases} 9s({}^{2}S_{1/2}^{}) \rightarrow 8p({}^{2}P_{1/2}^{0}), \ \lambda = 8.9 \ \mu\text{m} \\ 9s({}^{2}S_{1/2}^{}) \rightarrow 6p({}^{2}P_{3/2}^{0}), \ \lambda = 0.66 \ \mu\text{m} \end{cases}$   
3.  $AuO({}^{2}\Pi) + CSe({}^{1}\Sigma) \rightarrow Au^{*}(>6p({}^{2}P_{3/2}^{0}) + COSe({}^{1}\Sigma) + 5.97 \ \text{eV}: \text{ transitions are} \\ \begin{cases} 6p({}^{2}P_{3/2}^{}) \rightarrow 6s^{2}({}^{2}D_{5/2}^{}), \ \lambda = 0.312 \ \mu\text{m} \\ 6p({}^{2}P_{1/2}^{}) \rightarrow 6s^{2}({}^{2}D_{5/2}^{}), \ \lambda = 0.355 \ \mu\text{m} \end{cases}$ 

We note also the possibility of multistage lasing. In particular, one of the following ways of two-cascade ionization is possible for the first of the above examples:

$$6s(^{2}S_{1/2}) \xrightarrow{\lambda = 1,63\mu} 4p(^{2}P_{3/2}^{0}) \xrightarrow{\lambda = 9,55\mu} 3d(^{2}D_{5/2})$$

TABLE 3. Certain Catalysts (K - elements of the first group), Their Ground States, Thermal Effects of Reaction (2),  $E_2$  (in cm<sup>-1</sup>), Maximum Excitation Levels of the Catalysts Atoms, the Fuel (F), and the Binding Energy (eV) of the Catalyst Oxides E(K-O)

F K	CO( <sup>1</sup> Σ)	SO ( <sup>3</sup> Σ)	$CS(^{1}\Sigma)$	$CSe(^{1}\Sigma)$	E(K-O), eV
Li( <sup>2</sup> S <sub>1/2</sub> )	$\frac{16700}{2p(^2P^0_{3/2})}$	$\frac{18200}{2p({}^{2}P_{3/2}^{0})}$	28500 3s ( <sup>2</sup> S <sub>1/2</sub> )	<b>38700</b> 5s( <sup>2</sup> S <sub>1/2</sub> )	3.49
Na( <sup>2</sup> S <sub>1/2</sub> )	23800 3p( <sup>2</sup> P <sup>0</sup> <sub>3/2</sub> )	$25300 \\ 3p(^{2}P_{3/2}^{0})$	<b>35600</b> 5p( <sup>2</sup> P <sup>0</sup> <sub>3/2</sub> )	45800 Na <sup>+</sup>	2.61
K( <sup>2</sup> S <sub>1/2</sub> )	$\frac{28450}{4f({}^2F^0_{5/2})}$	29950 6p( <sup>2</sup> P <sup>0</sup> <sub>3/2</sub> )	40250 K <sup>+</sup>	<b>50450</b> К <sup>+</sup>	2.03
$Rb(^{2}S_{1/2})$	27400 4f( <sup>2</sup> F <sup>0</sup> <sub>5/2</sub> )	28900 6d( <sup>2</sup> D <sub>5/2</sub> )	<b>39200</b> Rb <sup>+</sup>	<b>49400</b> Rb <sup>+</sup>	2.16
Cs( <sup>2</sup> S <sub>1/2</sub> )	27550 9p( <sup>2</sup> P <sup>0</sup> <sub>3/2</sub> )	29050 11s ( <sup>2</sup> S <sub>1/2</sub> )	<b>39350</b> Cs <sup>+</sup>	<b>49550</b> Cs <sup>+</sup>	2.14
Cu( <sup>2</sup> S <sub>1/2</sub> )	22700 4s <sup>2</sup> ( <sup>2</sup> D <sub>3/2</sub> )	24200 4s <sup>2</sup> ( <sup>2</sup> D <sub>3/2</sub> )	<b>34500</b> 4p( <sup>2</sup> P <sup>0</sup> <sub>3/2</sub> )	<b>44700</b> 4p <sup>1</sup> ( <sup>2</sup> F <sup>0</sup> <sub>5/2</sub> )	2.74
Ag( <sup>2</sup> S <sub>1/2</sub> )	26300	27800	<b>38100</b> 5s <sup>2</sup> ( <sup>2</sup> D <sub>3/2</sub> )	<b>48300</b> 6s ( <sup>2</sup> S <sub>1/2</sub> )	2.29
Au( <sup>2</sup> S <sub>1/2</sub> )	26000 6s <sup>2</sup> ( <sup>2</sup> D <sub>3/2</sub> )	27500 6s <sup>2</sup> ( <sup>2</sup> D <sub>3/2</sub> )	<b>37800</b> 6p( <sup>2</sup> P <sub>1/2</sub> )	48000	2.33

Atoms of the first group of the table can thus be promising catalysts for chemical lasers operating in accordance with the first scheme (see Sec. 2).

A transition from the first excited state to the ground  $({}^2P_{1/2}^0 \rightarrow {}^2S_{1/2})$  in the considered elements, with exception of Cu and Au, is allowed (radiative times  $\simeq 10$  nsec). An exclusively important role is therefore assumed by the "radiation-drag" effect in the development of chemical lasers operating in the "donor-acceptor" scheme (see Sec. 2), where the intermediate electron-excited products serve as donors. The drag effect increases the effective lifetime  $\tau_{eff}$  of the donor by several orders of magnitude. Thus, for sodium D lines at sodium densities  $10^{14}-10^{15}$  cm<sup>-3</sup> we have  $\tau_{eff} \cong (10^2-10^3)$  rad. To ensure effective operation of the exchange laser, the following condition must be met:

$$\tau_{\rm ex} = (k_4 [A])^{-1} < \tau_{\rm qu}^{\rm D}$$
(9)

where  $k_4$  is the rate constant of the exchange process (4), [A] is the density of the acceptor (emitting) particles, and  $\tau_{qu}^D$  is the donor quenching time. The condition (9) determines the lower limit of the acceptor density in the mixture.

Table 4 lists certain atoms and molecules that can serve as acceptors in chemical lasers based on scheme 2; the donors are electron-excited atoms of the catalysts from the first group of the periodic table.

As to scheme (3) (Sec. 2), we note that its realization would blaze a new trail in the development of a chemical low-temperature source of resonant radiation (a narrow-band "chemical lamp") with wavelength from 0.34  $\mu$ m ( ${}^{2}P_{1/2}^{0} \rightarrow {}^{2}S_{1/2}$  transition in Ag) to 0.95  $\mu$ m ( ${}^{2}P_{1/2}^{0} \rightarrow {}^{2}S_{1/2}$  transition in Cs) (see [8-11] for details).

Spontaneous narrow-band radiation from a chemically reacting medium can be used as an optical pump source for solid, liquid, and gaseous media.

Catalyst (term), energy, cm <sup>-1</sup>	Acceptors (er resonant ener laser transit	mitting atoms or mole rgy level (term), ene tion, wavelength ( $\mu m$	cules), quasi- rgy dect (cm <sup>-1</sup> ), )
$Li(^2P^0_{1/2})$	Ni( <sup>1</sup> S <sub>0</sub> ); 175	$TiO(^{3}\Phi_{4}); 542$	$Li_{2}(A'\Sigma_{u}^{+}); 883$
14903.65	${}^{1}S_{0} \xrightarrow{3}{}^{3}D_{3}$	${}^{3}\Phi_{4} \rightarrow {}^{3}\Delta_{1}$ 0,9-1,2	$A^{1}\Sigma_{u}^{+} \rightarrow X^{1}\Sigma_{g}^{+}$
$Na(^{2}P_{1/2})$	Ni( <sup>3</sup> P <sub>0</sub> ); 938,9	BaO(A <sup>1</sup> $\Sigma^+$ ); 240	$Na_{2}(A^{1}\Sigma_{u}^{+}); 2280$
16956,18	${}^{3}P_{0} \rightarrow {}^{3}D_{3}$	$A^{1}\Sigma^{+} \rightarrow X^{1}\Sigma^{+}$	_
	0,634	0,7 – 0,9	$A^{1}\Sigma_{u}^{+} \rightarrow X^{1}\Sigma_{g}^{+}$
$K(^{2}P_{1/2})$	Fe( <sup>3</sup> F <sub>2</sub> ); 16,6	CaO(A' $\Sigma$ ); 1436	$K_{2}^{0,75-1,2}$ $K_{2}^{+}(A^{1}\Sigma_{u}^{+}); 1312$
12985,17	${}^{3}F_{2} \rightarrow {}^{5}D_{4}$	$A^1\Sigma \to X^1\Sigma$	$A^{1}\Sigma_{n}^{+} \rightarrow X^{1}\Sigma_{n}^{+}$
	0,772	1,15 - 1,5	u g 1,0 – 1,4
$\operatorname{Rb}({}^{2}\operatorname{P}_{1/2}^{0})$	Fe( <sup>3</sup> F <sub>3</sub> ); 18	$CaO(A'\Sigma)$ ; 1030	$Rb_2(b^3\Sigma_g); 100$
12579	${}^{3}F_{3} \rightarrow {}^{5}D_{4}$	$A'\Sigma \to X^1\Sigma$	$b^3 \Sigma_g^- \rightarrow X^1 \Sigma_g^+$
o (2−0 )	0,797	1,15 - 1,5	0,95 - 1,4
$Cs(^{2}P_{1/2}^{0})$	$Y(^{2}P_{1/2}^{0}); 649$	$SrO(A'\Sigma); 307$	$Cs_{2}(b^{3}\Sigma_{g}^{+}); 200$
11178,24	${}^{2}P_{1/2}^{0} \rightarrow {}^{2}D_{3/2}$	$\mathbf{A}'\Sigma \rightarrow \mathbf{X}'\Sigma$	$b^3 \Sigma_g^+ \rightarrow X^1 \Sigma_g^+$
Cu( <sup>2</sup> D <sub>5/2</sub> )	0,951 Gd( <sup>9</sup> F <sup>0</sup> <sub>5</sub> ),94	1,2 - 1,6 p SrO(A' $\Sigma$ ); 331	0,95 - 1,4
11202,57	${}^{9}F_{5}^{10} \rightarrow {}^{9}D_{6}^{0}$	$A'\Sigma \rightarrow X'\Sigma$	
$Ag(^{2}P_{1/2}^{0})$	1,04 Pb( <sup>1</sup> S <sub>0</sub> ); 85	1, 2 -1,6 CaO( $C^{1}\Sigma^{+}$ ); 790	SbO( $C^2\Delta_r$ ); -7
29552	${}^{1}S_{0} \rightarrow {}^{3}P_{1}$ 0,462	$C^{1}\Sigma^{+} - X^{1}\Sigma$ 0,4 - 0,5	$C^2 \Delta_r \rightarrow X^2 \Pi_r$ 0,36 - 0,42
$Au(^{2}D_{5/2})$	$I(^{2}P^{0}_{1/2}); 1558$		
9161,3	${}^{2}P_{1/2}^{0} \rightarrow {}^{2}P_{3/2}$		
	1,315		

TABLE 4. Potential Acceptors (emitting atoms or molecules) for Chemical Lasers with Chain Excitation Mechanism

One can consider, for example, the following scheme (Fig. 1). Gas is made to flow through a cell in which an oxidation reaction takes place in the presence of some alkali metal as a catalyst (Na atoms, for the sake of argument). During the chain reaction the sodium atoms are excited and emit on the D lines ( $\lambda_{D1}$  = 589.6 nm and  $\lambda_{D2}$  = 589 nm). The D-line radiation emerging from cell 1 drops to cell 2, through which is pumped gas containing Na atoms, a suitable acceptor, say Na<sub>2</sub> molecules, and a diluent. As a result, the radiation is resonantly absorbed by the Na atoms, followed by electron-electron (E-E) transfer of energy to the acceptors that are used as the laser particles:

$$Na + h\nu_{D1,D2} \rightarrow Na^{*}$$

$$Na^{*} + Na_{2} \rightarrow Na + Na_{2}^{*}$$

$$Na^{*}_{2} + h\nu_{1as} \rightarrow Na_{2} + 2h\nu_{1as}$$
(10)



↓ hν<sub>1</sub>

Fig. 1. Schematic realization of a narrowband "chemical lamp."

# 5. CHEMICAL-EXCIMER MECHANISM OF PUMPING LASERS ON ELECTRONIC TRANSITIONS

The prospects of developing a chemical-excimer laser are highly enticing. That this is feasible in principle was mentioned in Sec. 2. We have in mind here the possibility of using recombination reactions that produce laser particles in the form of the excimer complexes (5). One of the components participating in the triple collision is produced in an electron-excited state by purely chemical means.

It is known that the lower electronic state of two atomic molecules consisting of inertgas atoms (X = He, Ne, Ar, Kr, Xe) and alkali metals (K = Cs, Na, K, Li, Rb) is repulsive (disregarding the small Van der Waals minimum), a feature typical of excimer molecules. Formation of electron-excited states ( $A^2\Pi$  or  $C^2\Sigma^+$ ) of KX\* molecules followed by radiative decay can be described by the scheme

$$K^* + 2X \rightarrow KX^* + X$$

$$KX^* \rightarrow K + X + h\nu.$$
(11)

The bands  $A^2\Pi \rightarrow X^2\Sigma_{1/2}$  for various alkali metals range from 0.6 to 1.1 µm, the most intense bands being those of Xe. The  $C^2\Sigma^+ \rightarrow X^2\Sigma_{1/2}$  bands correspond to shorter wavelengths, 0.4-0.7 µm.

It is easy to estimate the threshold density of the NaXe excimer molecules (and hence the density of the electron-excited Na\* atoms) needed for lasing, say, at a threshold gain g<sub>thr</sub> =  $10^{-3}$  cm<sup>-1</sup>. Assuming a radiation wavelength  $\lambda_{rad} = 685$  nm (the A  $\rightarrow$  X transition), a band half width  $\Delta\lambda = 2.5$  nm, and a radiative decay time  $\tau_{rad} = 10$  nsec, we obtain from the relation

$$\sigma = \frac{1}{4\pi} \left( \frac{\ln 2}{\pi} \right)^{1/2} \left( \frac{\lambda^4}{C\Delta\lambda\tau} \right)$$
(12)

for the induced-transitions cross section [18] the estimate  $\sigma \approx 10^{-14} \text{ cm}^2$ . The threshold density of the excimer molecules is therefore  $N_{\text{thr}} \approx 10^{11} \text{ cm}^{-3}$ .

# 6. USE OF CHEMICAL REACTIONS WITH PARTICIPATION OF CLUSTER MOLECULES

Cobb et al. [16] reported for the first time experimental observation of visible light amplification by a chemically active medium. In the experiment, a supersonic stream of sodium vapor, containing the atomic component Na and the cluster molecules Na<sub>2</sub> and Na<sub>3</sub>, was mixed with a stream containing halogen (Br) atoms. A gain  $g = (2.5-5) \cdot 10^{-3} \text{ cm}^{-1}$  was recorded, with its maximum reached at the wavelength  $\lambda = 527 \text{ nm}$ . In their opinion, the weak-signal amplification corresponds to transitions of the sodium molecule Na<sub>2</sub>(B<sup>1</sup> $\Pi_u$ , v' = 5, 6  $\Rightarrow$  X<sup>1</sup> $\Sigma_g^+$ , v" = 13, 14), while the pumping of the upper (B, v') level and clearing of the lower one (X, v") follow the scheme

$$Na_3 + Br \xrightarrow{k_1} Na_2^*(B, v') + NaBr$$
 (13.1)

$$Na_{2}^{*}(B, v') \rightarrow Na_{2}(X, v'') + hv$$
 (13.2)

Na<sub>2</sub> (X, v<sup>'</sup>) + Br 
$$\xrightarrow{k_2}$$
 NaBr + Na (13.3)

Note that the experiments were carried out at very low working-gas densities (N  $\cong$  [Br]<sub>0</sub> < 10<sup>14</sup> cm<sup>-3</sup>). Obviously, for inversion to take place on the transitions Na<sub>2</sub>(B, v'  $\rightarrow$  X, v") it is necessary that the rate of the radiative population of the lower level (the process (13.2)) be lower than the rate of chemical deactivation of the lower working level (the process (13.3):

$$q_{\mathbf{v}'\mathbf{v}'} A < k_2 N, \tag{14}$$

where A is the Einstein coefficient (B  $\rightarrow$  X transition),  $q_V'v''$  is the Franck-Condon factor, and  $k_2$  is the rate constant of the chemical process (13.2). It follows from (14) that under the conditions of the experiments of [16] population inversion can be observed only for transitions with very low Franck-Condon factors. Indeed, for A  $\approx 10^8 \text{ sec}^{-1}$ , N  $\approx 10^{14} \text{ cm}^{-3}$  and the maximum value of the constant  $k_2 \approx 10^{-9} \text{ cm}^3/\text{sec}$  the factors are  $q_V'v'' \leq 10^{-3}$ . A sharply selective population of the upper laser level (B, v') is assumed here in the chemical process (13.1).

It was suggested in [17] that a chemical-excimer excitation mechanism can be realized under the conditions of the experiments of [16]. It was assumed that the radiating particle is the excimer complex  $Na_3Br^*$ . One of the indirect confirmations of this assumption is that the active-medium emission spectrum recorded in [16] has qualitative features perfectly analogous to the emission spectrum of excimer molecules [18]. According to [17], the kinetic scheme takes the form

$$Na_3 + Br \xrightarrow{K_1} Na_3 Br^*$$
(15.1)

$$Na_{3}Br^{*} \xrightarrow{f} Na_{2}^{*}(A, B, C) + NaBr(v)$$
 (15.2)

$$Na_{3}Br^{*} \xrightarrow{A} Na_{2} + NaBr + h\nu$$
(15.3)

$$Na_{a}Br^{*} + h\nu \rightarrow Na_{a} + NaBr + 2h\nu.$$
(15.4)

In process (15.1) there is formed a long-lived collisional complex  $Na_2Br^*$ , which can decay nonradiatively as in (15.2) with formation of electron-excited  $Na_2^*$  molecules and vibrationally excited NaBr(V) molecules, and by photon emission [Eq. (15.3)], a behavior typical of excimer molecules.

The equation for the population of the radiative state of the  $Na_3Br^*$  excimer is

$$\frac{d}{dt} [Na_{3}Br^{*}] = k_{1}[Na_{3}][Br] - (A + \gamma)[Na_{3}Br^{*}] - \frac{u}{d} [Na_{3}Br^{*}], \qquad (16)$$

where  $k_{\perp} = (1-2.5) \cdot 10^{-8} \text{ cm}^3/\text{sec}$  is the rate constant of the excimer formation (15.1),  $A \cong 10^8 \text{ sec}^{-1}$  is the spontaneous decay rate (15.3) of the excimer,  $\gamma$  [sec<sup>-1</sup>] is the nonradiative-decay rate, and the last term in (16) corresponds to removal of the excimer complex from the reaction zone ( $u \cong 6 \cdot 10^4 \text{ cm/sec}$  is the flow velocity,  $d \cong 0.5 \text{ cm}$  is the width of the reaction zone,  $u/d \simeq 10^5 \text{ sec}^{-1}$ ). In the stationary state we have for the excimer density

(1= /)

$$[Na_{a}Br^{*}] = k, [Na_{a}] [Br]/(A + \gamma + u/d)$$
(17)

Using relations (12)-(17) we obtain for the gain  $g = \sigma[Na_3Br^*]$ 

$$g = \frac{1}{4\pi} \left( \frac{\ln 2}{\pi} \right)^{1/2} \frac{\lambda^4}{c\Delta\lambda} k_1 [Na_3] [Br]$$
(18)

It is taken into account in (18) that  $A = \tau_{rad}^{-1}$  and  $A >> (\gamma + u/d)$ . Assuming  $\lambda = 527$  nm,  $\Delta\lambda = 1$  nm,  $[Na_3] \approx 2 \cdot 10^{13} \text{ cm}^{-3}$  and  $[Br] \approx 10^{14} \text{ cm}^{-3}$  (see [17]) we obtain for the gain the estimate  $g \approx (2-5) \cdot 10^{-3} \text{ cm}^{-1}$ , which agrees with the experimental data of [16]. Note that in this case the cross sections of the induced transitions are quite high,  $\sigma \approx 10^{-14} \text{ cm}^2$ , exceeding by two orders the cross section for ordinary excimers (the cross section for KrF\* is  $\sigma \approx 2 \cdot 10^{-16} \text{ cm}^2$  [18]).

The foregoing raises the natural question: is it possible, by starting from the simplest considerations (thermodynamic, energy-conservation law, Wigner-Witmer rule), to formulate a general premise capable of predicting chemical processes in which polyatomic molecules, radicals, or cluster formations participate and are potentially suitable for the development of chemical lasers for visible and near-infrared radiation?

Consider for simplicity the reaction of a triatomic molecule ABC with an atom D:

$$ABC + D \rightarrow AB + CD + Q \tag{19}$$

where Q is the heat of the reaction. Just as in the case of the triatomic sodium cluster [16] we consider hereafter initial triatomic molecules in which the A-B-C as well as the A-B binding energies are quite low.

In order that the reaction (19) ensure selective production of an electron-excited state AB\* it is necessary to satisfy the following conditions:

1) The reaction heat Q must be larger than the energy  $E(AB^*)$  of the electron-excited state and exceed substantially the binding energy D(AB) of the AB molecule in the electronic ground state

$$D(AB) < E(AB^{*}) < Q \tag{20}$$

2) The reaction heat Q does not exceed the energy  $E(CD^*)$  of the first electron-excited state of the product CD:

$$Q < E(CD^*)$$
(21)

3) The spin is conserved.

On the basis of these assumptions, we can restrict the group of triatomic molecules and their partners D, which can potentially act as reagents for chemical lasers on electronic transitions.

The reagents D can be halogen atoms (F, Cl, Br, I, At) or atoms of the oxygen subgroup (0, S, Se, Te, Po). In the general case D is an atom or a radical.

By way of ABC molecules we consider triatomic clusters  $A_3$ , aiming primarily at sufficiently low dissociation energies of the corresponding diatomic molecules in the electronic ground state, D(A-A) < 1.5 eV. We can single out here triatomic particles comprising alkalimetal elements (Li<sub>3</sub>, Na<sub>3</sub>, K<sub>3</sub>, Rb<sub>3</sub>, Cs<sub>3</sub>), alkaline-earth atoms (Be<sub>3</sub>, Mg<sub>3</sub>, Ca<sub>3</sub>, Sr<sub>3</sub>, Ba<sub>3</sub>), zinc-subgroup elements (Zn<sub>3</sub>, Cd<sub>3</sub>, Hg<sub>3</sub>), 3rd group elements (Al<sub>3</sub>, Ga<sub>3</sub>, In<sub>3</sub>, Tl<sub>3</sub>), and 4th group elements (Sc<sub>3</sub>, Ti<sub>3</sub>, V<sub>3</sub>, Cr<sub>3</sub>, Mn<sub>3</sub>, Fe<sub>3</sub>, Co<sub>3</sub>).

Table 5 lists some thermodynamic and spectroscopic data for diatomic clusters  $A_2$ . The following notation is used:  $A_2(...)$  is a molecule with the ground term indicated,  $D(A_2)$  is the dissociation energy (eV) of the molecule  $A_2$  in the ground state,  $R_e$  (in Å) is the internuclear distance of the ground electronic term,  $\omega_e$  (in cm<sup>-1</sup>) is the vibrational constant,  $A_2^*$  is the electron-excited state of the  $A_2$  molecule,  $R^*_e$  is the internuclear distance of

						t	
)@}#	A <sub>2</sub> (ground term)	D(A <sub>2</sub> ), eV	R <sub>e</sub> , A	$\omega_{e}, cm^{-1}$	Term $A_{2}^{*}$ , Te, cm <sup>-1</sup>	Term $A_2^*$ , $R_e^* A$ Te, cm <sup>-1</sup>	
Ι.	$\operatorname{Li}_{2}(X^{1}\Sigma_{g}^{+})$	1,03	2,6729	351,43	$(A^{1}\Sigma_{u}^{+})$ = I4068,35 $(B^{1}II_{u})$ = 20436 0I	3,108 2,935	(LiF) =5,94
2.	$\operatorname{Na}_{2}(X^{1}\Sigma_{g}^{+})$	0,74	3,0789		$(A^{T}\Sigma) = 14680,58 (B^{T}\Pi) = 20320,02$	3,638 3,423	(NaF) =4,95
3.	$K_2(X^1\Sigma_g^+)$	0,56	3,905	92,02	$(A^{1} \Sigma)$ = II68I,9 $(B^{1} \Pi)$ = I5376.74	4.23	(KF) =5,12
4.	$Rb_2(X^1\Sigma_g^+)$	0,43		57,31	$(A^{1} \Sigma)$ = II000 $(B^{1} \Pi)$ = 14662,6		(RbF) =5
5.	$Cs_2(X^1\Sigma_g^+)$	0,39	4,47	42,02	$(A^{1}\Sigma)$ $\cong 10000$ $(B^{1}\Pi)$ = 13043,88		(CsF) =5
6.	$\operatorname{Be}_{2}(X^{1}\Sigma_{g}^{+})$	~ 0,6			$(A^{1}\Sigma^{+}_{U}) \qquad \nu_{00} \sim 28000$	1	(BeF) =6,26
7.	$Mg_2(X^1\Sigma_g^+)$	0,05	3,891	51,12	$(A^{1}\Sigma_{u}^{+})$ 26068,76	3,082	(MgF) =4,77
8.	$Ca_2(X^1\Sigma_g^+)$	0,129	4.277	64,93	$(A^{1}\Sigma^{+}_{U})$ $\ll 18963$	3,8	(CaF) =5,5I
9.	$\operatorname{Sr}_{2}(X^{1}\Sigma_{g}^{+})$				1 <u>1</u> 1 <u>1</u>		$\frac{1}{1} = 5,6$
10.	$Ba_{2}(X^{1}\Sigma_{g}^{+})$	)		1	1 1 1 1		(BaF) = 5,4
II.	Zn <sub>2</sub>	~ 0,19	,2,35	1 1 1	1 1 1 1 1		(ZnF) = 3,7
12.	Cd <sub>2</sub>	~ 0,09	3,02	1	1 <u>1</u>		(CdF) = 3,2
13.	In <sub>2</sub>	1,04		1 ≈ 142 1	R and V shadowed bands ~ 18000	, ,	(InF) = 5,2
14.	Tl <sub>2</sub>	0,6		≈ 136	R – 1 shadowed bands 1 15500		(TIF) = 4,6
15.	$Pb_2(\widetilde{X}O_g^+)$	1,0	~ 3,08	= 109,8 1	$(CO_{u}^{\dagger})$ ! = I53IT ! ! (FO_{u}^{\dagger}) ! ! = I9807 !	3,0	(PbO) 1 = 3,86
16.		0,23	~ 3,8	1 ~ 89	absorption ! in region ! ~ 15000		(MnF) 1 = 4,4
17.	Fe <sub>2</sub>	1,06		1	$\nu_{00} = 18355$		(FeO) =4,2
	and the second						

TABLE 5. Some Spectroscopic Data for a Number of Diatomic Dimers  $\rm A_2$ ; Binding Energies of the Products AD

the excited electronic term, and E(AD) (in eV) is the binding energy of the product AD. From among the possible reactions (19) we chose those whose products AD had the largest binding energies in the ground state. The data were taken from [19-21]. Note that the binding energy in a ternary complex A<sub>3</sub> is lower than diatomic molecule A<sub>2</sub>, for example  $E(Li_2-Li) = 0.76$ eV,  $E(Pb_2-Pb) = 0.32$  eV.

Besides the substances listed in the table, one can cite a number of other diatomic AB molecules having low binding energies, namely the lanthanides  $(Nd_2-0.8 \text{ eV}, Sm_2-0.5, Eu_2 -0.5, Dy_2-0.7, Ho_2-0.8, Er_2-0.7, Tm_2-0.5, Yb_2-0.2)$ ; Ti<sub>2</sub>-1.3, Tb<sub>2</sub>-1.32; and the mixed compounds KCs-0.47, KRb-0.5, LiCs-0.72, NaCs-0.42, NaK-0.62, PbBi-1.4, TiBi-1.2.

Note that the binding energy of lanthanides with oxygen or fluorine atoms is  $E(A-D) \ge 6$  eV.

It follows from Table 5 that the first condition is met for practically all the listed substances (including the lanthanides). As for the second condition, it is not met for all substances — for diatomic clusters of elements from the second group of the periodic table (from Be<sub>2</sub> to Cd<sub>2</sub>, see Table 5) and Pb<sub>2</sub> the value of Te is practically equal to or less than the energy of the lower electron-excited AD\* state if halogens or oxygen-group atoms are used as oxidants.

The following reactions can take place in a mixture containing the components  $A/A_2/A_3$  and  $D/D_2$ :

$$A_{3} + D \xrightarrow{\uparrow} A_{2}^{*} + AD$$

$$A_{3} + A \xrightarrow{\uparrow} A + A(A^{*}) + AD$$
(22.1)

$$A_2 + D \rightarrow A(A^*) + AD \tag{22.2}$$

$$A_2^* \rightarrow A_2 + h\nu_1 \tag{22.3}$$

$$A^* \to A + h\nu_2 \tag{22.4}$$

$$A(A^*) + P_2 \rightarrow P + AP \tag{22.5}$$

$$A^* + A_2 \stackrel{\rightarrow}{\leftarrow} A + A_2^* \tag{22.6}$$

and a number of others. The process (22) is chainlike, the three channels (22.1)-(22.2) can lead to electronic excitation, and the additional pumping is effected in (22.6).

The alkali-metal subgroup satisfies the relations

$$E[A_{2}^{*}(A^{1}\Sigma_{u}^{+})] \leq E(A^{*}) \leq E[A_{2}^{*}(B^{1}\Pi_{u})],$$

where A\* is a lower electron-excited state  ${}^{2}P_{1/2,3/2}^{0}$  with an allowed transition. For the alkaline-earth element subgroup we have

$$E(A^*) \le E[A_2^*(A^1\Sigma_{11}^+)] \le E[A_2^*(B^1\Pi_{11})]$$

and A\* is the lower metastable electron-excited state  ${}^{3}P_{0,1,2}^{0}$ . It follows hence that from the standpoint of developing a laser operating on a transition with an upper level  $B^{1}\Pi_{U}$  for the first five substances (Table 5) and an upper level  $A^{1}\Sigma_{U}^{+}$  for substances numbered 6-10, its effectiveness will be lowered by the inverse process in (22.6). If, however, the upper level is an  $A^{1}\Sigma_{U}^{+}$  state of the alkali-metal subgroup, the effectiveness can be increased by the direct process in (22.6).

Substances numbered 7-12 and also  $Mn_2$  (Table 5) have anomalously low binding energy. In this respect they are close to inert gases, i.e., the lower state can be disrupted by the purely collisional process

$$A_{2}(v'' > 1) + M \rightarrow 2A + M - \Delta E, \qquad (23)$$

where  $\Delta E \leq (1-3)$  kT. Thus, in this case it becomes possible to develop a chemical laser similar to an excimer one.

The scheme of processes (22.1)-(22.6) with participation of cluster molecules is one of the possible ones. In principle, populations can be produced by the chemical-excimer mechanism, as noted above [see the processes (15.1)-(15.4)].

#### 7. CHEMICAL Na: BaO EXCHANGE LASER WITH CHAINLIKE EXCITATION

The operating principle of the hypothetical chemical Na:BaO laser on electronic transitions of the molecule BaO(A-X) is based on the use of a "donor-acceptor" scheme [8-11]. The role of the donor is assumed by an electron-excited sodium atom Na\*( ${}^{2}P_{j}$ ; j = 1/2,3/2), produced as an intermediate product in the chain reaction. The barium oxide BaO acts as an acceptor (a radiating laser molecule). The emission spectrum of the hypothetical Na:BaO laser has a range 0.7-1 µm corresponding to the transitions BaO(A<sup>1</sup>Σ<sup>+</sup>, v' → X<sup>1</sup>Σ<sup>+</sup>, v").

The pumping is by quasiresonant electron-electron (E-E) exchange:

Na<sup>\*</sup>(<sup>2</sup>P<sub>j</sub>) + BaO(X<sup>1</sup>Σ<sup>+</sup>, v') → Na(<sup>2</sup>S) + BaO(A<sup>1</sup>Σ, v') + 
$$\Delta E_{j}$$
  
(24)  
( $\Delta E_{1/2} = 233.9 \text{ cm}^{-1}$ ,  $\Delta E_{3/2} = 251.1 \text{ cm}^{-1}$  for v' = v'' = 0).

Experiment [13-15] has shown that sodium atoms in electron-excited states  $Na*({}^{2}P_{j})$  are produced in the oxidation chain reaction of carbon monoxide (CO) by nitrous oxide ( $N_{2}O$ ). The corresponding kinetic scheme can be represented in the form

$$\begin{cases} Na(^{2}S) \\ Na^{*}(^{2}P_{j}) \end{cases} + N_{2}O \\ \checkmark \\ NaO(^{2}II) + N_{2} + \begin{cases} 21,7 \text{ kcal/mole} \\ 70,1 \text{ kcal/mole} \end{cases}$$

We focus our attention below, in accordance with Sec. 2, on an initial mixture containing Na (a catalyst), CO (fuel),  $N_2O$  (oxidant), and He or Ar (diluent). It should be noted that the term "fuel" is used here figuratively, since the fuel itself is not decomposed in the considered chain reaction.

The principal kinetic scheme of the Na:BaO laser includes the following processes:

1. chain reaction with formation of electron-excited sodium atoms

$$\begin{cases} Na(^{2}S) \\ Na^{*}(^{2}P) \end{cases} N_{2}O \rightarrow NaO(^{2}\Pi) + N_{2} \\ NaO(^{2}\Pi) + CO \rightarrow \begin{cases} Na^{*}(^{2}P) \\ Na(^{2}S) \end{cases} CO_{2}; \end{cases}$$

2. breaking of the chain

$$NaO + \begin{cases} NaO \\ N_2O \end{cases} \rightarrow \begin{cases} Na_2O \\ NaO_2 \end{cases} + \begin{cases} O \\ N_2 \end{cases}$$

3. pumping (E-E exchange)

$$\operatorname{Na}^{*}({}^{2}\operatorname{P}_{j}) + \operatorname{BaO}(X^{1}\Sigma, v') \stackrel{\rightarrow}{\leftarrow} \operatorname{Na}({}^{2}\operatorname{S}) + \operatorname{BaO}^{*}(A^{1}\Sigma, v') + \begin{cases} 234 \text{ cm}^{-1}(D_{1}) \\ 250 \text{ cm}^{-1}(D_{2}) \end{cases} \end{cases}$$

4. spontaneous decay of Na\*(<sup>2</sup>P)

$$Na^{*}(^{2}P) \rightarrow Na(^{2}S) + h\nu_{Na};$$

5. trapping of radiation on D lines of the Na atoms  $Na^{*}(^{2}P_{i}) + \rho_{\nu}^{j} \neq Na(^{2}S) + 2\rho_{\nu}^{j}$ 

-	Atom	Al	Ga	Jn	 Tl
-	<sup>2</sup> P <sup>0</sup> <sub>3/2</sub>	112.06	826.24	2212.56	7792.7
Lnergy,	<sup>2</sup> S <sub>1/2</sub>	25347.76	24788.58	24372.87	26477.5
$\tau_{\rm sp}(^2S_1$	$/2 \frac{-2 P_{1/2}^{0}}{n \sec^{1/2}}$	20.0	20.4	17.9	16.0
$\tau_{\rm sp}(^2 {\rm S}_1^-)$	$/2 - {}^{2}P_{3/2}^{0}$	10.0	IO.9	9.8	14.2
$\sigma(^2 S_1 \\ 10^{12}$	$r_{1/2} - {}^{2}P_{3/2}^{0}$ cm <sup>2</sup>	3.25	5.62	10.1	<b>1</b> 5.5
$\lambda(^2S)$	$F_{1/2} - {}^2P_{3/2}^0$	,) <b>0.39</b> 6	0.417	0.451	0.535

TABLE 6. Conceivable Acceptor Atoms (radiating particles)



Fig. 2. Level scheme of lower electronic states of boron-subgroup atoms.

6. quenching of electron-excited atoms

$$Na^*(^2P) + M \rightarrow Na(^2S) + M$$

7. spontaneous decay of electron excited BaO\*(A) molecules

$$BaO^*(A^1\Sigma, v') \rightarrow BaO(X^1\Sigma, v'') + h\nu_{BaO};$$

8. quenching of electron-excited molecules BaO\*(A)

$$\dot{BaO}^*(A^1\Sigma, v') + M \rightarrow BaO(X^1\Sigma, v') + M$$

9. V-T relaxation of BaO(A, X) molecules

 $BaO^*(A^1\Sigma, v') + M \neq BaO^*(A^1\Sigma, v'-1) + M$ 

 $BaO(\dot{X}^{1}\Sigma, v'') + M \neq BaO(X^{1}\Sigma, v''-1) + M$ 

10. V-V exchange between BaO(A, X) molecules

$$BaO^{*}(A^{1}\Sigma, v') + BaO^{*}(A^{1}\Sigma, m') \neq BaO^{*}(A^{1}\Sigma, v'+1) + BaO^{*}(A^{1}\Sigma, m'-1)$$
$$BaO^{*}(A^{1}\Sigma, v') + BaO(X^{1}\Sigma, v'') \neq BaO^{*}(A^{1}\Sigma, v'+1) + BaO(X^{1}\Sigma, v''-1)$$
$$BaO^{*}(X^{1}\Sigma, v'') + BaO(X^{1}\Sigma, m') \neq BaO^{*}(X^{1}\Sigma, v''+1) + BaO(X^{1}\Sigma, m''-1)$$

11. electron-electron conversion  $BaO(A \leftrightarrow \Omega)$  $BaO^{*}(A^{1}\Sigma) + M \neq BaO^{*}(\Omega) + M$ 

 $(\Omega = a^3 \Sigma^+, b^3 \Pi_i, A^1 \Pi - \text{states});$ 

12. pulling processes between electron-excited BaO(A,  $\Omega$ ) molecules

$$BaO^{*}(A) + BaO^{*}(A) → BaO^{*}(Ω') + BaO(X)$$
  

$$BaO^{*}(A) + BaO(Ω) → BaO^{*}(Ω') + BaO(X)$$
  

$$BaO^{*}(Ω) + BaO^{*}(Ω) → BaO^{*}(Ω') + BaO(X)$$

13. spontaneous decay of molecules

 $BaO^{*}(\Omega, \Omega') \rightarrow BaO(X) + h\nu(h\nu')$ 

14. quenching of BaO\*( $\Omega$ ,  $\Omega$ ') molecules

$$\operatorname{BaO}^{*}(\Omega, \Omega') + M \to \operatorname{BaO}(X) + M$$

15. V-T relaxation of BaO( $\Omega$ ) molecules and V-V exchange between BaO(A,  $\Omega$ , X)

 $BaO^*(\Omega, n') + M \neq BaO^*(\Omega', n-1) + M$ 

$$BaO^{*}(\Omega, n') + \begin{cases} BaO^{*}(\Omega, n'') \\ BaO^{*}(X, v') \\ BaO^{*}(A, v') \end{cases} \stackrel{\stackrel{\checkmark}{\leftarrow}}{\leftarrow} BaO^{*}(\Omega, n'+1) + \begin{cases} BaO^{*}(\Omega, n''-1) \\ BaO^{*}(X, v'-1) \\ BaO^{*}(A, v'-1) \\ BaO^{*}(A, v'-1) \end{cases}$$

16. induced processes

A detailed analysis of the kinetics of the hypothetical Na:BaO laser and the choice, on its basis, of the kinetic constants, citing numerous experimental and theoretical studies, are given in [22]. Preliminary numerical calculations have shown that at an initial mixture pressure of several tens of torr ( $\cong$ 20-50 torr), depending on the initial molar composition of the Na|N<sub>2</sub>O|CO|BaO|He mixture, the gain for the working laser transitions BaO(A<sup>1</sup> $\Sigma$ , v' =  $O \Rightarrow X^{1}\Sigma$ , v'' = 5-10) can reach g<sub>0</sub>  $\cong$  (0.5-2.5)·10<sup>-3</sup> cm<sup>-1</sup>.

## 8. USE OF ATOMS AS ACCEPTOR (RADIATING) PARTICLES

The promise offered by the use, in "donor-acceptor" lasers, of boron-subgroup atoms (B, Al, Ga, Jn, Tl) as acceptor particles radiating on the  ${}^{2}S_{1/2} \rightarrow {}^{2}P_{3/2}^{0}$  transition was pointed out in [8-11]. The upper laser level can be pumped either directly in elementary oxidation chain reactions (in which case the atoms act as catalysts) or via E-E energy exchange with appropriate donors.

The donors, in particular, can be various diatomic molecules or radicals, with an electron excitation energy higher than  $25,000 \text{ cm}^{-1}$ .

A general systematic listing of diatomic donors suitable for use in chemical lasers on electronic transitions is given in [8-11]. Particularly distinguished are the compounds  $SiO(b^3\Pi_r)$ ,  $GeO(a^3\Pi_1, a^3\Sigma^+)$ ,

$$CS(a^{3}\Sigma, a^{3}\Pi_{r}), CSe(a^{3}\Pi), SiS(e^{3}\Sigma^{-}), SiSe(a^{3}\Pi_{i}), NO(a^{4}\Pi_{i}),$$

BF 
$$(a^3\Pi_r)$$
, AlF  $(a^3\Pi_r)$ , ACl $(a^3\Pi_r)$ , SiF $(a^4\Sigma^-)$ , GeF $(a^4\Sigma^-)$ .



Fig. 3. Additional acceptor-atom level scheme.

By now, reports have been published [23] of experimental registration of gain, in the pulsed regime, on electronic transitions of thallium atoms  $T1(7s^2S_{1/2} \rightarrow Gp^2 \ ^2P_{3/2})$  at a visible wavelength ( $\lambda = 5350$  Å). The  $T1*(7s^2S_{1/2})$  level was pumped by E-E exchange in collisions of thallium atoms with electron-excited silicon-oxide (SiO\*) or germanium-oxide.(GeO\*) molecules

$$\begin{cases} \text{SiO}^* \\ \text{GeO}^* \end{cases} + T \\ T \\ \end{bmatrix} \rightarrow \begin{cases} \text{SiO} \\ \text{GeO} \end{cases} + T \\ \end{cases}$$

The excited molecules were produced by chemical oxidation of Si or Ge by ozone  $0_3$ :

$$\begin{cases} Si \\ Ge \end{cases} + O_3 \rightarrow \begin{cases} SiO^* \\ GeO^* \end{cases} + O_2$$

The experiments of [23] are thus the first confirmation of certain previously reported [8-11] theoretical assumptions.

Table 6 lists some spectroscopic data on atoms of the boron subgroup. It contains the spontaneous-decay times of the electron-excited state  ${}^{2}S_{1/2}$  and the corresponding stimulated-transition cross sections (the cross sections were calculated for Doppler broadening at T = 300 K). These data permit an estimate of the minimum inverted-population density needed to obtain amplification. Thus, for a gain on the order of  $10^{-3}$  cm<sup>-1</sup> in the  ${}^{2}S_{1/2} \rightarrow {}^{2}P_{3/2}^{0}$  transition it suffices to produce an inversion density  $\Delta N \simeq 10^{8}$ - $10^{9}$  cm<sup>-3</sup>.

The principal level scheme for the lower electronic states for atoms of the boron subgroup is shown in Fig. 2. Here 1 is the lowest state of the laser transition (the 0-1 transition is forbidden), and 2 is the upper state (to 0-2 transition is allowed). A transition from the ground state 0 to the state 3 is forbidden.

An important process for effective laser operation is rapid clearing of the lower laser level. In the case considered, such are the quasiresonance exchange processes E-E, E-V, E-VR, E-R, E-RT, E-VRT. For the boron-subgroup atoms the role of quasiresonant deactivators can be assumed by many molecules (e.g.,  $H_2$ ,  $D_2$ ,  $N_2$ ,  $N_2$ 0, CO, NO, and others), and also by certain atoms. For the low-lying states 1 (for example, for boron B in aluminum Al), the effective E-T line is deactivation.

The deactivation of the lower level can be described in the form

		A	$\frac{1(3p - {}^{2}P^{0})}{1}$	2)In	$(5n - 2p^0)$	)
	A B	$(2p - {}^{2}P_{1/2}^{0})$	G	$a(4p - {}^{2}P_{1/2}^{0})$	1/2	$T_{1}(6p - {}^{2}P_{1/2}^{0})$
(n -	$-1)p - {}^{2}P_{3/}^{0}$	2 I5,254	112,06	826,24	2212,56	7792,7
	$ns - {}^{2}S_{1/2}$	40039,65	25347,76	24788,58	24372,87	26477,5
	$np - {}^{2}P_{1/2}^{0/2}$	48613,6	32949,80	33044,06	31816,61	34159,9
	$np - {}^{2}P_{3/2}^{0}$	48613,6	32965,64	33155,03	32114,79	35161,1
•	M, process	He, E-T	He, E-T	$H_2, E-R(J = 0)$	CO, E-V	I, E-E
	$\Delta E$ , cm <sup>-1</sup>	15,254	112,06	17,2	69,2	189,6
	λ <sub>1</sub> , μm	0,250	0,396	0,417	0,451	0,535
	λ <sub>2,1/2</sub> ,μm	I,166	1,315	1,211	1,343	1,302
-	λ <sub>2,3/2</sub> ,μm	, 1,166	1,313	I,195	1,292	1,152

TABLE 7. Additional Data on the Boron-Subgroup Elements

$$A^{*}[(n-1)p({}^{2}P^{0}_{3/2})] + M \to A[(n-1)p({}^{2}P^{0}_{1/2})] + M(E, V, R, T) + \Delta E$$
(25)

where M is the collision partner and  $\Delta E$  is the energy defect. Table 7 lists additional data, including information on the possible partners that can deactivate the lower working states of boron-subgroup atoms. The choice of the components M is dictated by the requirement that the energy defect  $\Delta E$  be a minimum. It can be seen from the table that in all cases  $\Delta E < kT$ .

One can consider in principle two-cascade lasing on atomic transitions, say on the transitions  $3 \rightarrow 2 \rightarrow 1$  (Fig. 2). In this situation the level 3 is pumped by E-E energy exchange with a specially chosen chemically produced donor. In particular, to pump the level  ${}^{3}P({}^{2}P^{0}_{j=(1/2),(3/2)})$  of the boron atom it is advantageous to use as a donor the electron-excited metastable state of nitrogen  $N_{2}^{*}(A^{3}\Sigma_{u}^{+})$ , or else  $CO({}^{3}\Pi_{r})$ . The most suitable donor for pumping the upper states  $Al[4p({}^{2}P_{p}^{0})]$ ,  $Ga[5p({}^{2}P_{j}^{0})]$ ,  $In[6p({}^{2}P_{j}^{0})]$  and  $Tl[7p({}^{2}P_{j})]$  is the NO\*( $a^{4}\Pi_{i}$ ) molecule.

A particular case of the scheme of Fig. 2 is a variant in which the level 1 is the ground term (this scheme is shown in Fig. 3). The working laser transition is  $3 \rightarrow 2$ , and the lower level 2 is cleared by radiative decay. The orbital momentum  $L_1$  of the ground state (level  $l_1$ ) either coincides with the orbital momentum  $L_3$  of the third level, or it differs (level  $l_2$ ) by 2 (i.e.,  $|L_1 - L_2| = 2$ ). The transitions  $2 \rightarrow 3$  and  $1 \rightarrow 2$  are thus allowed, while  $1 \rightarrow 3$  is forbidden. In principle, most atoms of the periodic table can operate in accordance with such a scheme, limited only by the energy of the corresponding donors. For example, for the alkali-metal subgroup the levels  $l_1$  and 3 can be the terms  $ns^{-2}S_{1/2}$  and  $(n + 1)s^{-2}S_{1/2}$ , and the level 2 can be the term  $np^{-2}P^0(j = 1/2, 3/2)$ . For the beryllium subgroup,  $ns^{2-1}S_0$  and  $(n + 1)s^{-1}S_0$  correspond to levels  $l_1$  and 3, respectively,  $np^{-1}P_1^0$  to level 2, etc.

## 9. THE QUESTION OF INCREASING THE ATOM DENSITIES

A timely task of the considered problem is to obtain a sufficiently high density of atoms of various elements in the gas phase.

In fact, for most elements the saturated vapor pressure at a temperature 500 K is negligibly low [24]. Two variants can be proposed here.

1) In the first, a suitable element is introduced as an additive into the solid, liquid, or gaseous fuel. When certain fuels are burned, the energy released suffices to heat the products all the way to  $T \cong 2000-3000$  K, i.e., above the boiling points of many elements. This mixture is then passed through a suprsonic nozzle and cooled to room temperature and below. The vapor pressure of the element added to the fuel can exceed in the supersonic stream the equilibrium pressure by many orders.

2) The second variant is based on the fact that the boiling temperatures of many organometallic compounds of volatile hydrides of elements and of other compounds are low (500 K [24-26]). It is therefore natural to use these compounds, decompose them by discharge, photolysis, or heating, and obtain an atomic component in gaseous form. Here are a few examples:

a) carbonyls of metals [26], which have evaporation temperatures from 30°C for Ni(CO)<sub>4</sub> to 210°C for  $Ir_4(CO)_{12}$ , boiling temperatures from 43°C for Ni(CO)<sub>4</sub> to 175°C for W(CO)<sub>6</sub>, and decomposition temperatures from 50 to 500°C;

b) volatile hydrides of the subgroup elements of hydrogen, nitrogen, and fluorine with boiling temperatures substantially below 100°C (with the exception of water) [25];

c) organoelemental compounds, the boiling temperatures of which do not exceed 200-300°C, for example [24]:

	,,	r(	CH <sub>3</sub> ) <sub>2</sub> SnI	H CH(	CH <sub>3</sub> ) <sub>2</sub>	Bi(CH <sub>3</sub> )	3	
Hy- dride Z	n(CH <sub>3</sub> ) <sub>2</sub>	Ga(CH <sub>3</sub> )	3 İ	Hg (CH <sub>3</sub> )	2		Pb (CH <sub>3</sub> ) 4	In (CH <sub>3</sub> ) <sub>3</sub>
Boil- ing temp.,	44	56	59	92	106	110	110	136

## 10. CONCLUSIONS

We have presented here certain results of exploratory investigations carried out in the quantum-radiophysics and optics laboratories of the Lebedev Physics Institute of the USSR Academy of Sciences. Principal attention was paid to a new class of chemical lasers operating on electronic transitions of atoms, radicals, or molecules, excited by oxidation chain reactions in the presence of catalysts. Results are presented of calculations of the amplification properties of a conceivable chemical Na:BaO laser. A number of other questions have also been analyzed (the possibility of using atoms as radiating particles, the chemicalexcimer mechanism, the use of cluster complexes in the reactions, and others).

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