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Soviet Chemical Laser Research: Pulsed Lasers

Yuri Ksander



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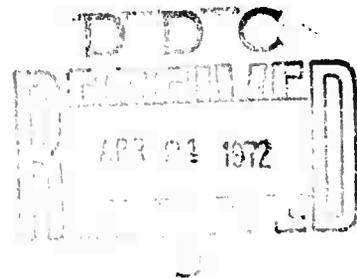
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| 10. ABSTRACT Reviews Soviet work on pulsed chemical lasers published in the open literature in 1963-1970. Whereas U.S. research combines the approaches of physics, quantum electrodynamics, and aerodynamics, Soviet laser research is heavily--and expertly --oriented to understanding the chemical reactions. They prefer pulsed to cw systems, remain staunch protagonists of chain branching lasers, and experiment with fewer gas mixtures. Tal'roze's Chemical Physics Institute group, which built the first workable Soviet HF laser system in 1969, concentrates on kinetics of vibrationally excited diatomic systems, as does Dolgov-Savel'yev's Nuclear Physics Institute group. Basov, at the Lebedev Institute, also committed to HF systems, has studied gas lasers with discharge, photolytic, and other initiation. Khokhlov at Moscow State University is refining research on HN3+CO2 mixtures and studying means of controlling reaction rates by resonant coupling and selective heating. Pekar in the Ukraine proposed a laser based on photorecombination of atoms. | | 11. KEY WORDS Lasers Chemistry USSR--Science Bibliography | |

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PREFACE

This report was prepared as part of a continuing study of selected areas of Soviet science and technology within the Advanced Research Projects Agency sponsored Rand Project -- Soviet Literature Exploitation. The materials reviewed in this paper were published in Soviet open-source literature over the period from 1963 to 1970.

A preliminary version of this report was distributed to members of the Rand-ARPA Chemical Laser Panel in February 1971.

SUMMARY

The Soviet laser community supports five mutually exclusive research groups in the field of chemical lasers.

Tal'roze's group at the Chemical Physics Institute and Dolgov-Savel'yev's group at the Nuclear Physics Institute are primarily involved in the study of kinetics of vibrationally excited diatomic systems. Studies of chain branching as a laser mechanism are highly favored by these groups. To Tal'roze goes the credit for building the first Soviet workable HF system in 1969.

Basov's group at the Lebedev Institute is also committed to predominantly HF systems. In addition to these, $H_2 + Cl_2$ and $HN_3 + CO_2$ mixtures have been studied with discharge, photolytic, and other initiation.

Khokhlov at the Moscow State University appears to be refining much of Basov's research on $HN_3 + CO_2$ mixtures. His group is studying means for controlling chemical reaction rates by way of resonant coupling of laser radiation to a substance and subsequent selective heating.

Pekar at the Semiconductor Physics Institute of the Ukrainian Academy of Sciences has proposed a chemical laser based on photo-recombination of atoms.

In general, the bulk of Soviet research is analytical, seeking solutions to problems concerning stability of reagents, mixing rates and triggering. Pulsed systems appear to predominate over cw systems, although analytical models of the latter have been developed.

The Soviets appear to have a reasonably well-balanced chemical laser research program heavily populated by chemists, which although rich in expertise, manpower and resources, is more academically oriented than the U.S. effort.

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I. INTRODUCTION

The first seven years (1960-1967) of the first laser decade were truly "the age of discovery." Everyone's efforts during those years were devoted to screening potential laser candidates and seeking new laser wavelengths. Lasers based on dielectric materials came out first (1960) and were followed by those based on gaseous mixtures and glasses (1961) and on semiconductors (1962). The concept of a chemical laser was demonstrated experimentally two years later (1964). Monoatomic gaseous and the solid-state media gave way to, although were not replaced by, molecular beam mixtures (1964) and liquids (1966 -- chelates, organic dyes, and inorganic acids).

By 1967, nearly the entire laser R&D appears to have undergone a maturation process as a result of which emphasis was shifted from innovations to design optimization of the existing technology. The most outstanding exception to this evolution is, perhaps, the chemical laser field where, although considerable strides have been taken to build "ultimate" high-energy devices, the search for new materials goes on. It is generally conceded that the chemical laser technology as a whole is not far enough advanced, and a number of basic -- and extremely valuable -- measurements is badly lacking.

The purpose of this paper is threefold: First, effort will be made to outline the recent Soviet work on chemical lasers as reflected in the open-source literature; second, to identify those problems which the Soviets have addressed extensively; and third, to bring up to date those U.S. researchers who normally must rely on badly outdated translations and to stimulate their interest in the Soviet literature exploitation studies.

11. THE LEADERSHIP AND PHILOSOPHY OF THE SOVIET EFFORT

A. Whereas in the United States some two dozen institutions -- both Government and private -- are actively engaged in the chemical laser research, the Soviets have fielded five research teams only. Each team is headed by a prominent member of the Soviet laser community, with the rank of Academician or a Corresponding Member. The group leaders and their affiliations are as follows:

1. V. L. Tal'roze at the Chemical Physics Institute AN SSSR
2. N. G. Basov at the Lebedev Institute
3. R. V. Khokhlov at the Moscow State University
4. G. G. Dolgov-Savel'yev at the Institute of Nuclear Physics, Siberian Branch AN SSSR
5. S. I. Pekar at the Institute of Semiconductors AN UkrSSR

B. In general, the U.S. open-source literature abounds in materials on new developments and applications of lasers which show considerable promise for both civilian and military uses. By contrast, Soviet publications and authors are traditionally reticent in fully discussing the real technological advances. Instead, laser work in the USSR gives an impression of being more academically oriented than in the United States.

Yet, considering the number of contributing authors in the laser field (≈ 1600 in 1970) and, in many instances, their prominence in the Soviet science, the Soviets have clearly and consciously established a strong and viable laser R&D base. From this base they are capable of launching a concentrated effort to attain any national goal, once it has been identified important to their economy or prestige. Although they have not as yet achieved significant breakthroughs in chemical lasers, the Soviets have recognized this field as potentially promising and they have diverted into it considerable expertise, manpower, and resources.

C. The rule-of-the-thumb of the Soviet chemical laser research is thorough understanding of the mechanisms of chemical reactions. In this connection, the Soviets have staffed the above groups with expert

chemists. In so doing, they have departed from the American approach which utilizes the combined talents of essentially the physicists, quantum electronics engineers, and aerodynamicists.

D. The purists among the Soviet laser researchers are generally reluctant to use the term "chemical laser." They feel that the existing devices hardly qualify for that name since the trigger energy required to set off the chemical reaction is in excess of the energy stored in the system. They are willing to go along with the charade, insofar as the production of the population inversion in such systems is a result of an elementary process of chemistry.

E. Except for this didactic assertion, the Soviet researchers are generally aware -- and accept -- the following basic constraints of a chemical laser system:

1. Reagent Stability

They all agree that one of the important features of a chemical laser is the stability of reagents. Ideally, one would want to consider chemicals which, when mixed, react slowly, if at all, until triggered. This eliminates production of undesirable free radicals (such as F in an HF system);

2. Mixing Rates

Introduction of stably mixable reactants into the cavity should be leisurely, thus ensuring average cw powers from a device of a reasonable size. More rapid filling results in an essentially flowing laser which, although capable of greater pulsed power output, suffers nevertheless from poor beam quality;

3. Triggering

In such an ideal laser triggering should occur on command, and the energy required to trigger the reaction should be smaller than the energy stored in the system. In addition to being modest, the initiation energy should be uniformly distributed in the pulse.

In general, the Soviets have experimented with fewer gas mixtures than the Americans, and the HF system which appears to be potentially high-yield -- although not without problems -- remains the most studied lasing specie in both countries.

III. BRANCHED CHAIN REACTIONS

The cornerstone of the Soviet chemical laser research was laid by chemists like N. N. Semenov. With their knowledge of the overall chemical and photochemical aspects of chemical reactions, they were able to convince the majority of the merits of branched chain reactions. Today, the discussion of the branched (and simple) chain reactions as laser mechanisms is more than generously treated in the Soviet open literature.¹⁻⁶ In fact, these reactions are so dear to the Soviet laser heart that the authors get generally carried away and fail to publish the pertinent experimental results.

No attempt will be made here to add to this tired subject. It should be mentioned, however, that the American and Soviet views on the merits of "chain-branching" lasers have never been fully reconciled. The Soviets remain staunch protagonists of branched chains while the Americans (notably Pimentel) have studied them with reservations. Briefly, the Soviet arguments in favor of branched reactions are:

- A. high sensitivity to small changes in the temperature and density of a system;
- B. rapid (exponential) reaction rates;
- C. maximum population inversion independent of initiation energy.

The above arguments postulate a laser which uses practically no external energy to initiate the reaction and which effectively couples the chemical reaction energy to laser energy. In fact, claims of electrical and chemical efficiencies of 2-10% and 0.2-2%, respectively, were made by the Tal'roze group in 1969.⁷

IV. VIBRATIONALLY EXCITED SYSTEMS

A. THE CHEMICAL EFFICIENCY

Tal'roze's derivation of the chemical laser efficiency for the case of electronic excitation of the cw oscillation was presented in Ref. 4. The case of the vibrationally excited population inversion is discussed below.

The equations for the field in the resonator and the population inversion are, respectively:

$$\frac{dn}{dt} = \alpha W(t) - K_r n - \sigma I n; \quad \frac{dI}{dt} = \sigma I n c - \frac{I}{\tau_{res}} \quad (1)$$

where $n = n_2 - n_1$ is the difference in level populations;

n_2, n_1 is a pair of vibrational-rotational levels 2 and 1;

$\alpha W(t)$ is the rate of producing a population inversion in the chemical reaction;

$$\alpha W = (\alpha_2 - \alpha_1) W;$$

W is the total rate of production of reaction products in all states;

α_1 is the effectiveness of producing i-th state in the elementary act;

σ is the stimulated transition cross section;

I is the coherent optical flux in the resonator in photons/cm².sec

$\tau_{res} = L/c (f_t + f_a)$ is the photon lifetime;

L is the resonator length;

f_t and f_a are the coefficients of transmission and absorption of light at the mirror;

c is the velocity of light;

K_r is the rate of vibrational deexcitation (the same for levels 1 and 2), which in the case of total inversion is determined by the rate of vibrational transfer ($K_r = K_{v-v} N$; where K_{v-v} is the rate of vibrational transfer and N is total concentration of the "working" particles in all the states).

The solution of (1) is made under the assumption that the system returns to steady state in a time shorter than the chemical reaction time

$$I(t) = f_t \left[\frac{\alpha W(t) L}{f_t + f_a} - \frac{K_r}{\sigma} \right] \quad (2)$$

and the threshold reaction rate is

$$W_t = \frac{K_r (f_t + f_a)}{\alpha \sigma L} \quad (3)$$

In the case of a stationary chemical reaction (i.e., where $W(t)$ and K_r are constant, such as the case may be in a flowing system), the chemical efficiency is

$$\kappa = \frac{f_t}{f_t + f_a} \frac{q}{\Delta H} \left[\alpha - \frac{K_r (f_t + f_a)}{\sigma L M} \right] \quad (4)$$

where q and ΔH are, respectively, the amount of energy evolved due to the working transitions and in the formation of a single molecule. The dependence of κ on W is shown in Fig. 1, where W_t is the threshold reaction rate and κ_{lim} is the limiting efficiency.

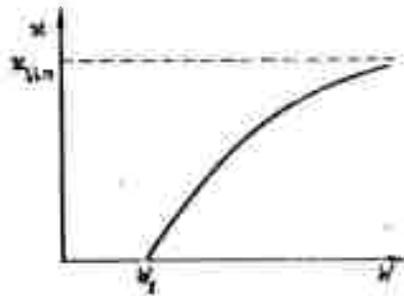


Fig. 1. Dependence of Chemical Efficiency on W

In the case of a pulsed reaction with a total inversion of the final product initiated at a time $t = 0$

$$K_r = K_{v-v} N = K_{v-v} \int_0^t W(t) dt \quad (5)$$

and the laser intensity (from (2)) is

$$I(t) = f_t \left[\frac{\alpha L M(t)}{f_t + f_a} - \frac{K_{v-v}}{\sigma} \int_0^t W(t) dt \right] \quad (6)$$

The generation occurs before time t_0 for which (for a given $W(t)$) the expression inside brackets becomes zero. The chemical efficiency then becomes

$$\kappa = \frac{f_t}{f_t + f_a} \frac{\alpha q}{\Delta H} \frac{\int_0^{t_0} \left[W(t) - \frac{K_{v-v}(f_t + f_a)}{\alpha \sigma L} \int_0^t W(\tau) d\tau \right] dt}{\int_0^{\infty} W(t) dt} \quad (7)$$

In the case where relaxation $K_{v-v} = 0$ and $t_0 \rightarrow \infty$, the limiting value of efficiency is

$$\kappa_{lim} = \frac{f_t}{f_t + f_a} \frac{\alpha q}{\Delta H} \quad (8)$$

In the case of a branched chain reaction, the expression for the generation time, intensity and chemical efficiency are as follows:

$$t_0 = -\frac{1}{\phi} \ln(1 - a\phi) \quad (9)$$

$$I(t) = \frac{f_t}{f_t + f_a} \alpha L W_0 \left[e^{\phi t} \left(1 - \frac{1}{a\phi} \right) + \frac{1}{a\phi} \right] \quad (10)$$

$$\kappa_{bc} = \kappa_{lim} \frac{W_0}{\phi \int_0^{\infty} W(t) dt} \left[-\frac{\ln(1 - a\phi)}{a\phi} - 1 \right] \quad (11)$$

where ϕ is the branching factor.

When $a\phi \geq 1$, Eqs. (9) and (11) cease to hold, t_0 increases and is determined by the consumption of reagents. When $a\phi \ll 1$, Eqs. (9) and (11) are as follows:

$$t_0 = a \left(1 - \frac{a\phi}{2} \right) \quad (12)$$

$$\kappa_{bc} = \kappa_{sc} \left(1 + \frac{2}{3} a\phi \right) \quad (13)$$

where κ_{sc} is the chemical efficiency of a simple chain reaction.

The dependence of κ on ϕ (Eq. (11)) clearly shows the effect of chain branching on the attainment of a limiting chemical efficiency (Fig. 2).

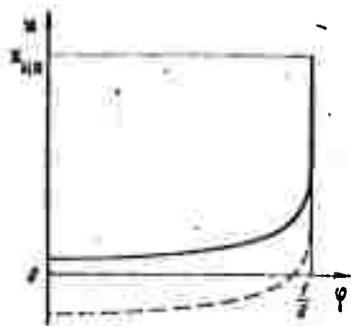


Fig. 2. Dependence of chemical efficiency on branching factor (from Eq. (11)). Dotted curve for $W_o v < W_t$.

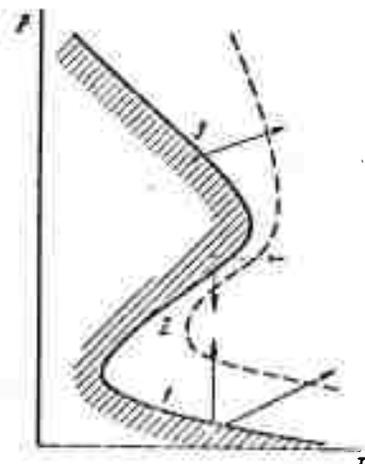


Fig. 3. Explosion limits for HF mixtures. Arrows indicate possible "routes" achieving "branched" generation.

The chemical efficiency η increases rapidly also with temperature, since $\phi \sim \exp(-E/RT)$. The analysis shows that intense generation in a branched reaction is achieved at temperatures and pressures which are well inside the ignition limits, while the shaded area constitutes a region of relative inactivity (Fig. 3).

The existence of the first and second ignition regions in the branched reactions occurring in HF mixtures was established by Semenov and Shilov.⁸ The third region was postulated subsequently by Tal'roze for $H_2 + F_2$ mixtures with O_2 .⁹

B. DIATOMIC SYSTEMS

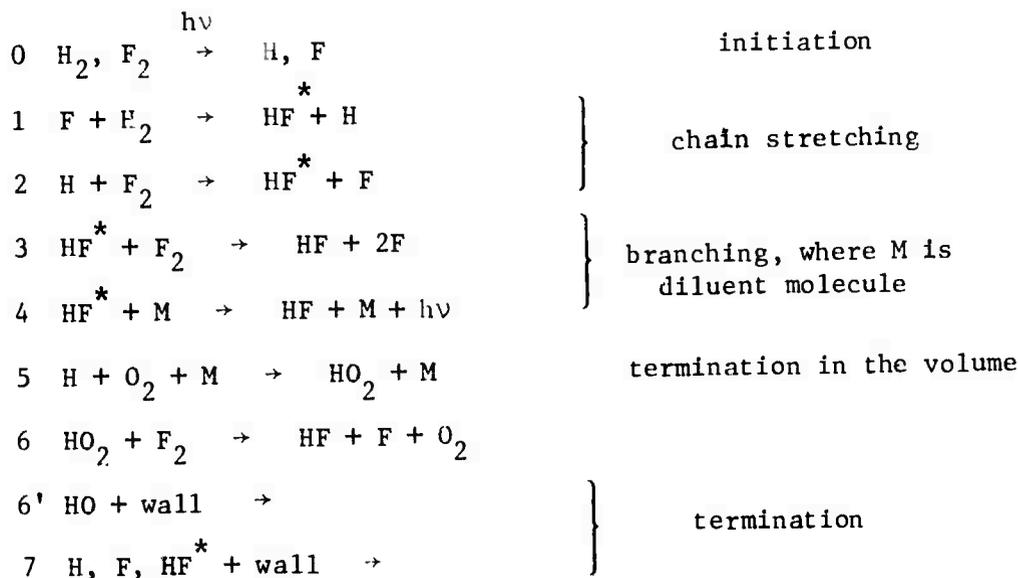
1. Mixtures with Discharge Initiation

a. H_2, F_2 Experiments

By the time Pimentel's $UF_6 + H_2$ laser was rolled-out in 1965, Tal'roze, who by that time had inherited Semenov's mantle at the Chemical Physics Institute, and Orayevskiy at the Lebedev Institute, concluded that the most efficient way of building purely chemical lasers was via branched chain reactions. Although Pimentel's 1965 laser was hailed as "principal achievement,"⁵ the feeling at CPI was that the low chemical efficiency of such a laser was the result of an improper choice of a mixture in which self-sustaining reactions -- even simple ones -- were clearly impossible.* Nevertheless, during the next four years, CPI's researchers were unable to deliver -- short of a continued criticism of

* $UF_6 + H_2 = UF_5 + F$
 $F + H_2 = HF^* + H + 32\text{kcal/mole} \dots \dots \text{(weak reaction)}$
 $UF_5 + ^2H_2 = UF_5H + H \dots \dots \dots \text{endothermic, no chain}$

American systems -- a workable HF system. Finally, in 1969, Tal'roze's group managed to produce generation within both the first^{3,7} and second¹⁰ ignition limits, based on the following reactions:



In his experiments, Tal'roze used a pulsed electric discharge which not only increased the temperature of the mixture but also provided a ready source of initiating active centers for the reaction. The trigger pulse duration was ~1 μsec and the pulse energy ~2j, i.e., an energy which was approximately one-half the energy stored in the system. His experimental setup is shown in Fig. 4.

The experiments were carried out at pressures near the first ignition region ($P_{H_2} \approx P_{F_2} \approx 2 - 4$ torr) in a tube 80 cm long¹⁰ and at higher pressures ($P_{H_2} \approx P_{F_2} = 30$ torr and $P_{O_2} = 10$ torr) in a tube 20 cm long.³ The fluoride windows in the tubes² were at Brewster angles and the optical cavity, in the case of the 80 cm tube, consisted of one spherical gold-sputtered mirror and one plane polished germanium plate which served as the output mirror. In the case of the shorter tube, the cavity consisted of confocal gold-sputtered mirrors, one of which had a 3-mm diameter aperture for the beam extraction. A Ge:Au detector (time constant $\sim 10^{-6}$ sec) was used at the output of an IR-monochromator in the case of the 80-cm tube. A slightly faster detector (time constant $\sim 10^{-7}$ sec) was used directly in the second case. The total optical energy was measured calorimetrically. The observation of chemiluminescence

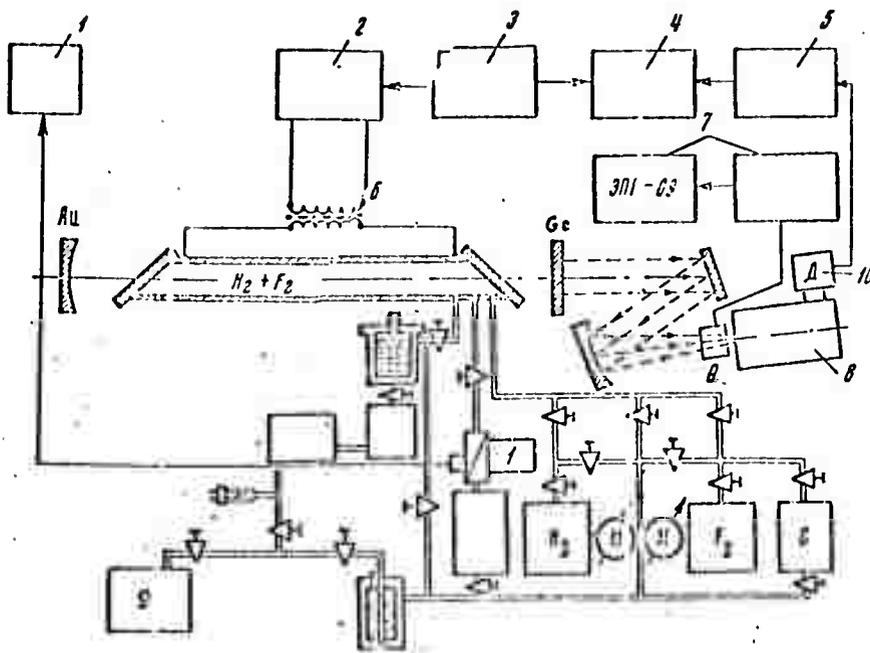


Fig. 4. Experimental Setup. 1 - manometer; 2 - hv pulse generator; 3 - startup pulse generator; 4 - oscillograph; 5 - broad band amplifier; 6 - pulse transformer; 7 - measuring devices; 8 - IR monochromator; 9 - vacuum pump; 10 - detector; Q - calorimeter.

was done by way of covering the distant (from the detector) mirror. The generation was in the $3600-4200\text{ cm}^{-1}$ range, which would seem to indicate a total vibrational population inversion in the HF molecule.

A series of oscillograms obtained in the experiments with the 80-cm tube is shown in Fig. 5. The oscillograms in column a show the IR chemiluminescence and those in columns b and c -- generation, taken at smaller amplifications (1/100) and scanned at much shorter rates (1/10). Those under b and c indicate a rapid rise in the intensity and in the leading and lagging slopes of the pulse which are characteristics of generation. Also clearly noticeable is the attainment of the generation peak before the chemiluminescence maximum.

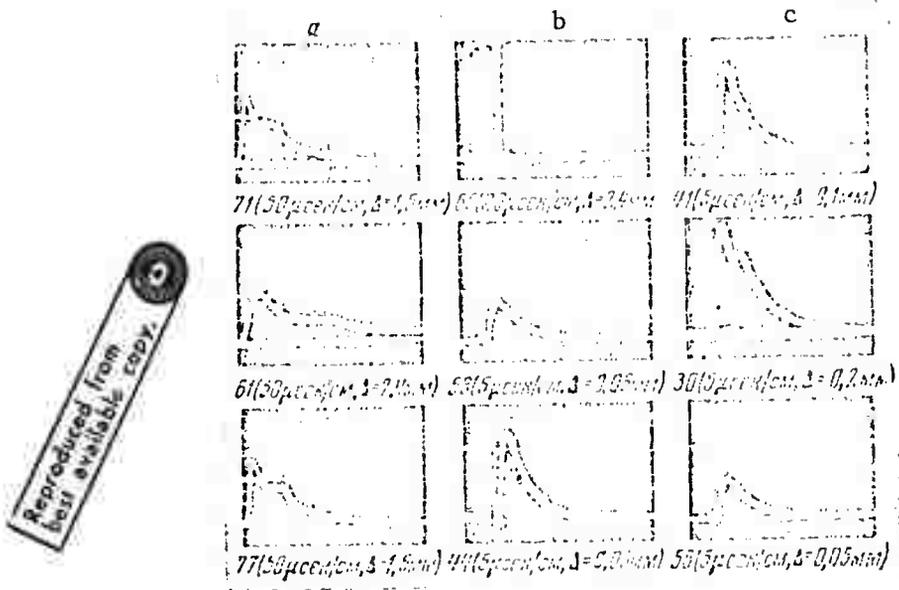


Fig. 5. Oscillograms of (a) chemiluminescence (b and c) generation; Δ is the slit width.

The generation pulses in the first (Fig. 6) and second (Fig. 7) tubes are shown below at maximum scanning rates.

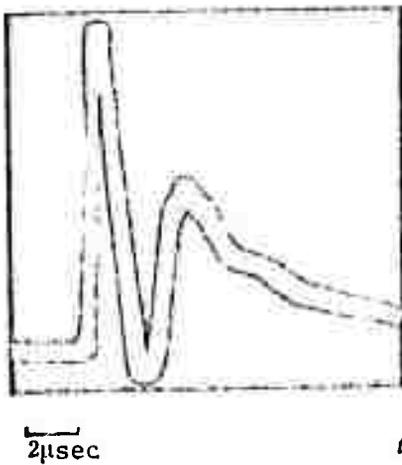


Fig. 6. Generation pulse in the 80-cm tube at $P_{H_2} \approx P_{F_2} \approx 2-4$ torr

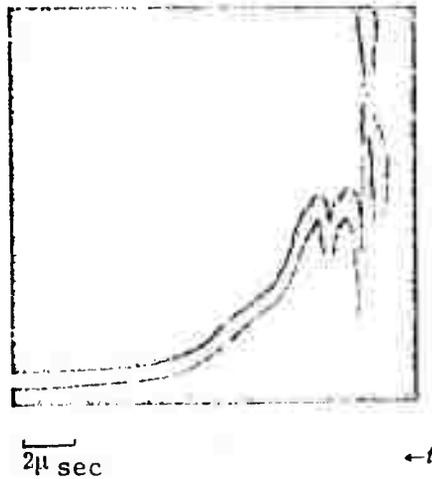


Fig. 7. Generation pulse in the 20-cm tube at a $P_{H_2} \approx P_{F_2} = 30$ torr, $P_{O_2} = 10$ torr

The total energy (measured calorimetrically) in the first tube at low pressures was 30 - 70 mj. The accuracy of the absolute measurement

was not greater than a factor of 2. Based on this, the calculated value of chemical and electrical efficiencies were 0.2-2% and 2-10% respectively.

Using the IR chemiluminescence method, Tal'roze calculated the HF reaction rates for the lower ignition limit.* The reaction rate based on a $\tau = 10^{-4}$ sec chemiluminescence pulse was $\sim 10^{21}$ cm³/molecule.sec. This favorably agrees with the value calculated from $W = K_1(H_2)n_o$, where $n_o \approx 10^{15}$ cm³ is the initial concentration of F atoms in the discharge, i.e., $W = 10^{-11} \times 10^{17} \times 10^{15} = 10^{21}$ cm³/molecule.sec.

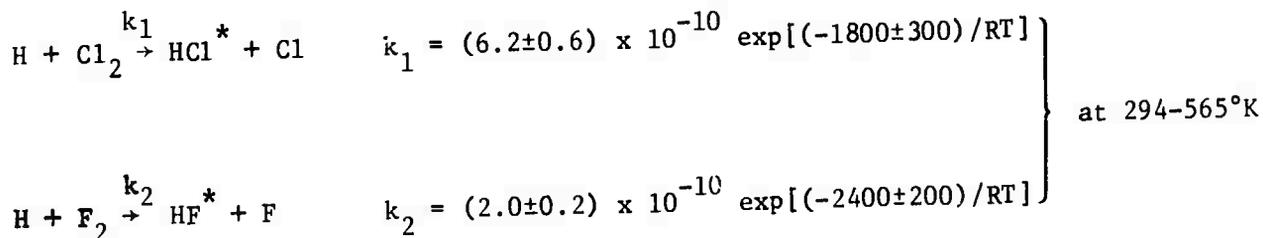
i. Effect of Branching

The effect of branching on the reaction rate is considerable. The branching constant inside the ignition "peninsula" is $\phi \approx \sqrt{2K_2K_3} |F_2|$, where $|F_2|$ is the absolute concentration of F₂. Thus,

$$\phi \approx 6 \times 10^{-14} |F_2| \exp(-1500/RT)$$

which shows that near the lower ignition limit $\phi \approx 10^4 \text{ sec}^{-1}$ and branching contributes to efficiency only on the order of one percent; at higher pressures, near the upper ignition limit $\phi \approx 10^5 \text{ sec}^{-1}$ and the rate of branching intensifies.

*Using mass-spectroscopic methods (based on probing the diffusion cloud in a flow), Tal'roze claims to have measured accurately the absolute rates for the overall reactions in H + Cl₂ and H + F₂ systems; these are in cm³/molecule.sec. 11

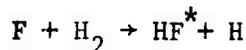
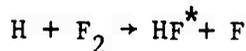


Thus, Tal'roze's $H_2 + F_2 + O_2$ explosion laser was capable of short use pulses with the peak power on the order of 10 kw and the chemical efficiency of up to 2%. Tal'roze feels that these results can be improved further by way of providing for a more uniform distribution of reaction in the tube and having the generation occur over a large volume. This can be done using mixtures whose p & T parameters are well above the second ignition limit.

ii. Spectral Composition

No provision was made in Tal'roze's work to look at the beam spectrum in detail, although several weak $1 \rightarrow 0$ vibrational transitions of the HF molecules were observed. Basov¹² and Dolgov-Savel'yev¹³ who looked more closely at the spectral structure of an $H_2 + F_2$ laser, failed inexplicably to observe the $1 \rightarrow 0$ transitions. Basov did, however, show that the laser emission in such a mixture originates from very high (6th and lower) vibrational levels, the greatest number of transitions occurring between $2 \rightarrow 1$ and $5 \rightarrow 4$ bands.

The large number of $5 \rightarrow 4$ transitions may be enhanced by depopulation of the $v = 4$ level due to reaction $HF(4) + F_2 \rightarrow HF(0) + 2F$. The cross section of such a reaction is greater than that of similar processes involving molecules with $v > 4$. The high intensity of $2 \rightarrow 1$ transitions could be the result of a highly populated level 2 by the products of either one of the following reactions:¹



It is also conceivable that the $v = 1$ level becomes depopulated rapidly as a result of $HF_{v=1}$ collisions with the hydrogen. At this stage, Basov's¹² and Tal'roze's¹³ findings appear contradictory. Tal'roze's conjecture that Basov's inability to observe generation due to $1 \rightarrow 0$ transitions was hampered by the presence of some HF(0) molecules in the mixture prior to the reaction, appears to be reasonable.

2. Mixtures with Photolytic Initiation

a. MoF_6 , UF_6 , $\text{F}_2:\text{H}_2$ Experiments

The mechanism of the HF production is more complex in the case of electric discharge initiation than for flash photolysis. The experiments in the Dolgov-Savel'yev laboratory were conducted on fluorine compounds (MoF_6 , UF_6 , F_2) mixed with H_2 .^{13,14} The experimental setup is shown in Fig. 8.

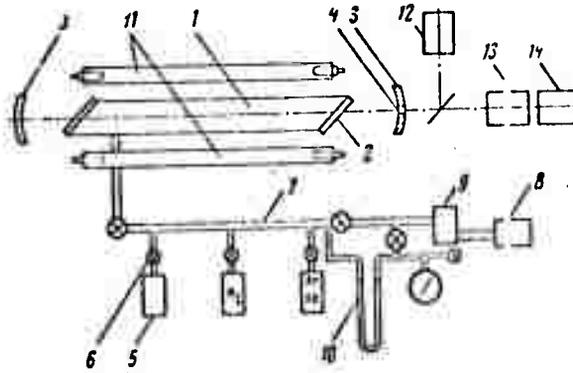


Fig. 8. Experimental setup. 1 - quartz tube; 2 - fluorite windows; 3 - spherical mirrors; 4 - aperture; 5 - gas tank; 6 - needle nozzle; 7 - mixing chamber; 8 - vacuum pump; 9 - nitrogen traps; 10 - oil manometer; 11 - IFP-20000 flashlamps; 12 - detector; 13 - IKM-1 monochromator and Ge: Au crystal; 14 - IEK-1 calorimeter.

A quartz tube 60 cm long and 1 cm in diameter with fluorite Brewster-angle windows was used. Optics consisted of external spherical ($R=200$ cm) gold mirrors. The power was extracted through a 0.2-cm (dia.) aperture. The mixture was introduced into the tube through non-corrosive (copper, teflon, stainless steel) vessels, and the system was evacuated down to 3×10^{-2} torr. The trigger pulse was provided by two IFP-20000 lamps operating in two regimes: 1) "long" pulse (250 μsec , 2.5 kJ capacitor energy at 4 kv) and 2) "short" pulse (10 μsec , 250 j at 20 kv). Output detection was by means of a Ge: Au detector (at 77°K). The spectral

composition was observed with an IKM-1 monochromator (8cm^{-1} slit) and another Ge:Au crystal. The energy was measured calorimetrically using an IEK-1 instrument.

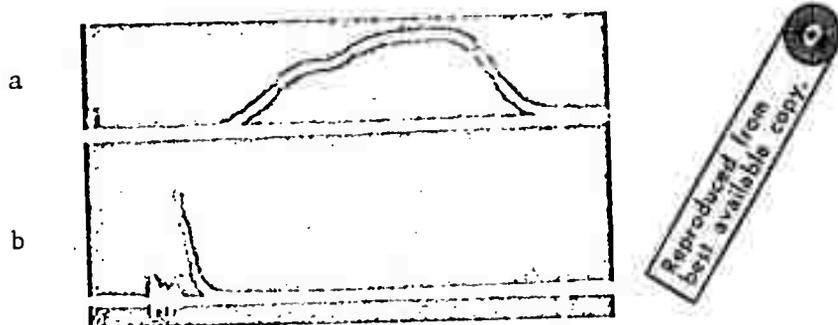
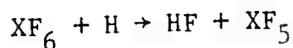
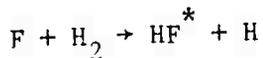
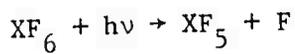


Fig. 9. Generation in the $\text{XF}_6 + \text{H}_2$ mixture. $P_{\text{H}_2}/P_{\text{XF}_6} = 2$;
 $P_{\text{XF}_6} = 10$ torr. (a) "long" pulse, 60 μsec total scan
 (b) "short" pulse, 140 μsec total scan.

The following photolytic reactions were studied:



where X = Mo or U. Figure 9 shows generation in the $\text{XF}_6 + \text{H}_2$ mixture triggered by "long" and "short" pulses. In the case of "long" pulses, the mixture had to be changed completely after each firing, since subsequent flashes failed to produce laser pulses. In the case of "short" pulse initiation, multiple (10-15) laser pulses could be obtained from the same mixture, although the per pulse power decreased progressively for each flash. When the XF_6 pressure was increased ($P_{\text{H}_2}:P_{\text{F}_2} = 2$), the energy saturation was fairly rapid and this was attributed to depopulation of the upper vibrational levels of HF^* molecules -- responsible for the branching -- by XF_6 molecules in the $\text{XF}_5 + \text{F} \rightarrow \text{XF}_6$ type reaction (Fig. 10).

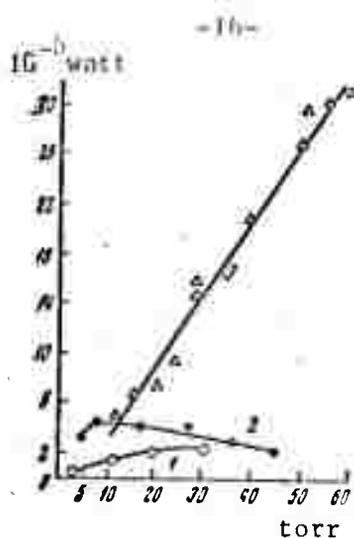


Fig. 10. Dependence of output energy on fluoride pressures.
 $P_{H_2}/P_{XF_6} = 2$; $P_{H_2}/P_{F_2} = 1$ (1) $UF_6 + H_2$ (2) $MoF_6 + H_2$ (3) $F_2 + H_2$

i. Effect of Buffer Gas

The effect of buffer gas (Ar and Xe) on the output energy is shown in Fig. 11. The increase in the output energy for small additions of buffer gas was due to the rise in the specific heat of the system and to increased relaxation of the V-R state. Further additions of a buffer gas (in excess of 8 torr) decrease the output energy as a result of a chemical reaction taking place between fluorine and the inert gas.

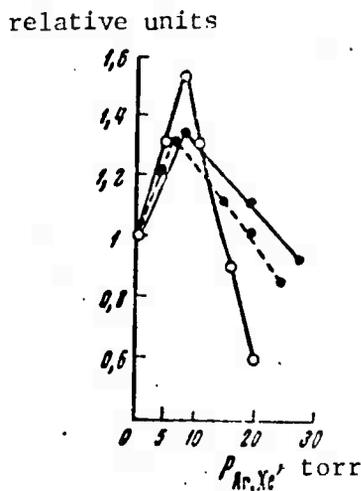


Fig. 11. Dependence of output energy on buffer gas pressures in $XF_6 + H_2$. \circ -- Xe, \bullet -- Ar; solid curve -- $P_{MoF_6} = 8$ torr; dotted curve -- $P_{MoF_6} = 4.5$ torr.

ii. Spectral Composition

The spectral analysis showed that the generation was due to vibrational-rotational transitions $P_{2,1}(4)$ ---- $P_{2,1}(7)$ (Fig. 12).

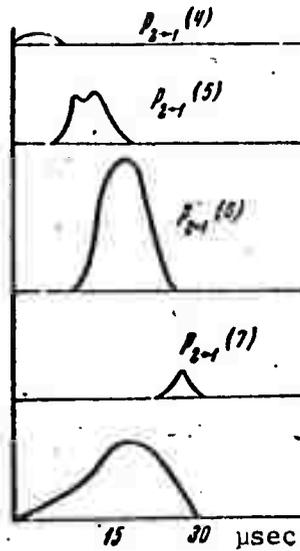


Fig. 12. Spectral composition of emission from $\text{XF}_6 + \text{H}_2$.

Similar experiments with the $\text{F}_2 + \text{H}_2$ mixture were conducted and the effect of short pulse flashing on the output energy is shown as curve 3 in Fig. 10. The spectral composition of the beam showed transitions from very high vibrational bands ($\text{P}_{3 \rightarrow 2}$ (4) — $\text{P}_{3 \rightarrow 2}$ (8) and $\text{P}_{2 \rightarrow 1}$ (5) — $\text{P}_{2 \rightarrow 1}$ (13)). However, as was also the case in Basov's experiments,²² no $1 \rightarrow 0$ transitions occurred (Fig. 13).

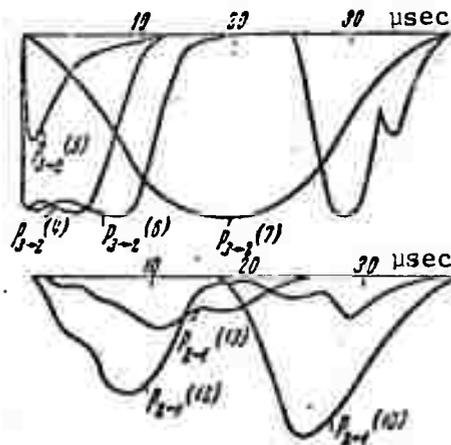


Fig. 13. Spectral composition of emission from $\text{F}_2 + \text{H}_2$

In the case of "long" trigger pulses, the pump power was small and the laser pulse rose almost exponentially, while lagging the former by $\sim 60 \mu\text{sec}$ (Dolgov-Savel'yev refers to this as an "induction" period, Fig. 14).

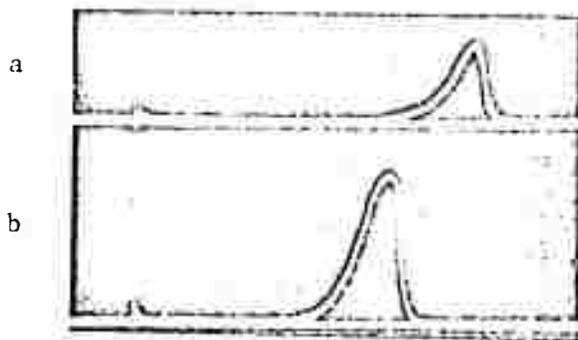


Fig. 14. Generation of $H_2 + F_2$ under "long" excitation. $P_{H_2} = P_{F_2}$. Total scan 140 μ sec. (a) $P_{F_2} = 5$ torr ; (b) $P_{F_2} = 12$ torr

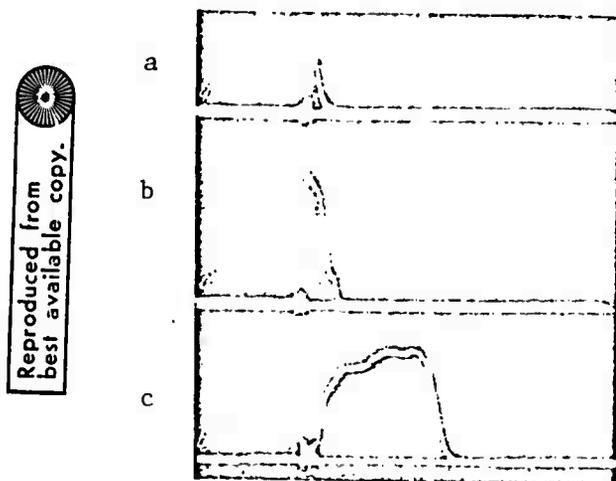


Fig. 15. Generation of $H_2 + F_2$ under "short" excitation. Total scan 140 μ sec. (a) First (b) Tenth (c) 30th pulses.

This occurs because the number of photodissociated fluorine atoms is insufficient to produce the necessary number of HF^* molecules for the population inversion. This situation becomes remedied shortly thereafter and the ensuing chain branching reaction causes an exponential growth of the laser pulse. The departure from the exponential pulse shape is due to the continuing photolysis of fluorine which causes an increase in the production rate of HF^* molecules. Assuming that HF^* molecules are produced as a result of chain branching reaction, the reaction rate was calculated from the oscillograms in Fig. 14 and was

equal to 5×10^5 — 10^6 sec^{-1} .

The onset of a quasi-cw regime (Fig. 15) was due to a decrease in the reaction rate as a result of deexcitation of HF ($v \geq 3$) by the resonator field. The sharp termination of the laser pulse was due to a transition from the chain reaction regime to the thermal explosion.

iii. Quantum Yield

The quantum yield (HF^*/F) was determined for the $F_2 + H_2$ mixture under "short" pulse pumping. First, the flashlamp energy was measured in the 2800-3800 Å range (F_2 absorption) and equaled 0.4j. Since the lamp spectra in this region are linear, the coefficient of absorption of F_2 was assumed constant and equal to $0.4 \text{ atm}^{-1} \cdot \text{cm}^{-1}$. The extracted energy was measured at the total pressure of 40 torr and at equal partial pressures. At this pressure the ratio of stimulated emission energy to absorbed energy was 10 and the quantum yield was 100. However, the total energy output with respect to the energy stored in the capacitors was considerably less than unity (i.e., chemical efficiency less than 1%). The accuracy of these results is doubtful considering that the energy was extracted through a 0.2 - cm dia. aperture and that the entire cavity was assumed to be uniformly filled with the mixture.

b. H_2, Cl_2 Experiments

i. Spectral Composition

The vibrationally-inverted HCl was studied by Basov and co-workers¹⁵ on a setup identical to the original Kasper-Pimentel experiments. The time histories of pumping and laser pulses are shown below:

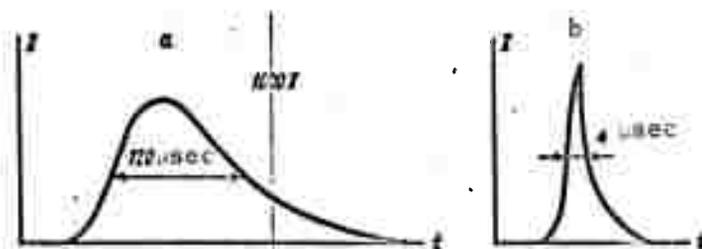


Fig. 16. Temporal dependence of (a) pumping pulse; (b) generation line 2652 cm^{-1} . $P_{Cl_2} = 15 \text{ torr}$, $P_{H_2} = 40 \text{ torr}$; $T = 300^\circ \text{K}$.

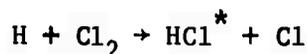
In contrast with the Kasper-Pimentel experiments in which the oscillation was attributed to the $1 \rightarrow 0$ vibrational transitions, Basov's work identified the $2 \rightarrow 1$ transitions as the responsible mechanism.

Pimentel's findings were unacceptable to Basov in view of the earlier statements of Polanyi that total vibrational inversion in the $H + Cl_2 \rightarrow HCl^* + Cl$ reaction is due to the $2 \rightarrow 1$ and $3 \rightarrow 2$ transitions. In order to explain the $1 \rightarrow 0$ transitions one must incorrectly assume, Basov claims, a rather rapid attainment of the Boltzmann distribution of vibrational levels. Basov's experimental discovery of the $2 \rightarrow 1$ transitions, appears to lift this contradiction, and according to him, is significant to the gain calculations.

ii. Effect of Anharmonicity

The departure from Boltzmann distribution of vibrational levels is caused, apparently, by anharmonicity of molecules. Calculations to determine the real energy-level distribution and the gain in anharmonic oscillators -- such as the HCl molecule -- were carried out recently by Gordiyets et al.¹⁶ The study model was an $H_2 + Cl_2$ chemical laser with photoexcitation. Normally, the nonstationary equations for the HCl vibrational level population must be solved concurrently with the chemical kinetic equations which define the rates of production and extinction of the HCl molecules at various vibrational levels. This approach was reportedly taken by Igoshin and Orayevskiy who, using numerical methods, obtained useful -- although not very reliable -- data concerning the temporal picture of the pump intensity and its effect on the population inversion.¹⁷ However, the usefulness of the Igoshin-Orayevskiy study is limited insofar as their findings pertain to only the initial stage of the reaction, characterized by the v-v relaxation. Another serious limitation of the same study was its restriction to the five lower levels of HCl.

Gordiyets's interest in the higher levels was fueled essentially by the molecule's anharmonicity. The following reaction was considered:



Western data were used to find the relative rates for the above reaction

and the following two models were considered:

a) the vibrational energy released in the reaction was 40% of the total energy ($\alpha_0 = 0$, $\alpha_1 = 0.134$, $\alpha_2 = 0.482$, $\alpha_3 = 0.362$, $\alpha_4 = 0.022$, $\alpha_{n \geq 5} = 0$).

b) the vibrational energy portion -- 10% ($\alpha_0 = 0.7559$, $\alpha_1 = 3.2 \times 10^{-2}$, $\alpha_2 = 1.185 \times 10^{-1}$, $\alpha_3 = 8.9 \times 10^{-2}$, $\alpha_4 = 5.7 \times 10^{-3}$ and $\alpha_{n \geq 5} = 0$).

The chemical kinetic and the relaxation equations were solved concurrently on a computer for nine HCl levels and by way of the nonstationary heat conduction equation. The rate of energy liberation per unit volume of gas was derived from the following formula:

$$W = - \sum_{m=0}^8 [E_1 - (m-1)\Delta E] m \left(\frac{dX_m}{dt} \right)_{\text{coll}} + \left[\sum_{m=0}^8 \alpha_m \{ E_{\text{chem}} - [E_1 - (m-1)\Delta E] \} \right] k_{11} N_H N_{Cl_2} + [h\nu - D_{Cl_2}] A t e^{-\alpha} N_{Cl_2} \quad (14)$$

where $(dX_m/dt)_{\text{coll}}$ is the rate of collisional relaxation of the m-th level of the HCl molecule and can be calculated from the relaxation equations, i.e.,

$$\left(\frac{dX_m}{dt} \right)_{\text{coll}} = \frac{dX_m}{dt} - (A_{m+1,m} X_{m+1} - A_{m,m-1} X_m + B_m - C_m X_m); \quad (15)$$

where E_{chem} is the total energy of reaction; $h\bar{\nu}$ is the average photon energy absorbed by Cl_2 (~3.8 eV); D_{Cl_2} is the dissociation energy of Cl_2 ; N_H and N_{Cl_2} are the concentrations of H and Cl_2 molecules; k_{11} is the reaction constant.

The third term in Equation 14, defines the production of "hot" Cl atoms during the photodissociation of Cl_2 molecules. The effect of this term on the reaction rate is significant. The results of calculations for a tube with a 1.7-cm radius and a 300°K wall temperature are shown graphically in Figs. 17-23.



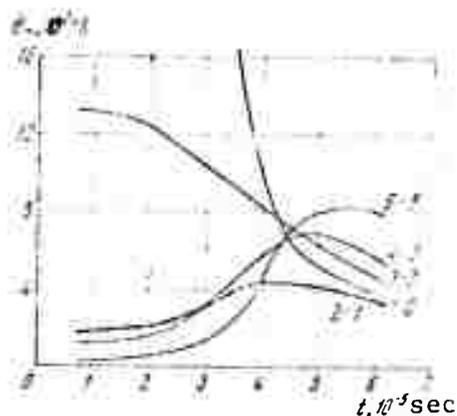


Fig. 17. Temporal variation of effective vibrational temperatures for different pairs of HCl levels in the course of a chemical reaction (original mixture: 1 torr Cl_2 + 1 torr H_2 + 10 torr He, $A = 10^9$, $\tau = 10^{-4}$ sec).

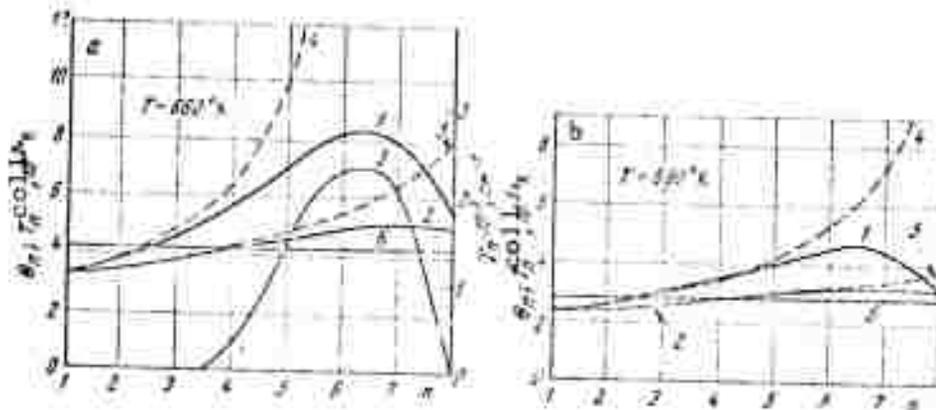


Fig. 18. Dependence of θ_n (curve 1), T_n^{coll} (curve 2) and v_n (curve 3) on the HCl level number in a chemical reaction (original mixture parameters same as in Fig. 17). Curves 4 & 5 -- temperatures θ_n and T_n^{coll} for the Treanor* distribution. Curves 6 -- temperature for a harmonic oscillator model with the same amount of vibrational energy: (a) --40% of chemical energy converted into vibrational, $t = 6 \times 10^{-5}$ sec; (b) --10%, $t = 5.8 \times 10^{-5}$ sec.

*Treanor, C. E., J. W. Rich, and R. G. Rehm. J. Chem. Phys., 48, 1798, 1968.

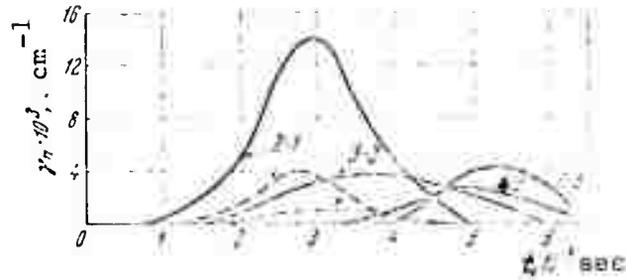


Fig. 19. Temporal variation of gain ν_n for various pairs of HCl levels (original mixture parameters same as in Fig. 17). Solid and dotted curves respectively correspond to 40% and 10% chemical energy conversions into vibrational energy.

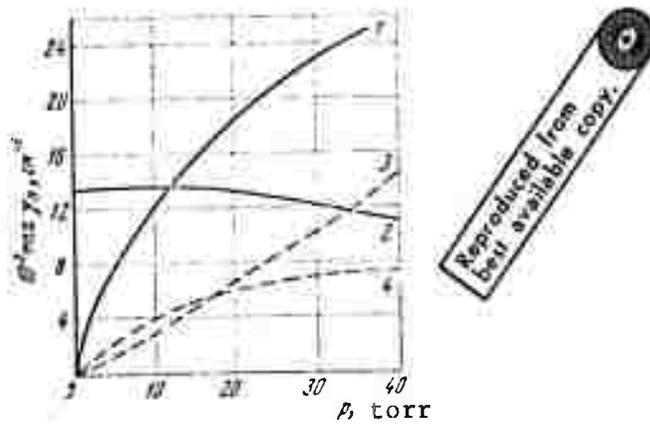


Fig. 20. Dependence of gain $\max \nu_2$ (curves 1 & 2) and $\max \nu_6$ (curves 3 & 4) on total pressure (curves 1 & 3) for $\text{Cl}_2 + \text{H}_2 + \text{He}$ mixture at 1:1:10 and on partial He pressure (curve 2 & 4) for a mixture with the same parameters as Fig. 17.

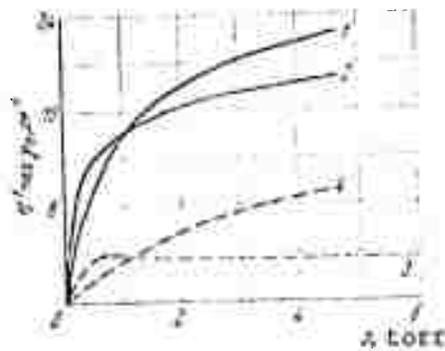


Fig. 21. Dependence of gain $\max \nu_2$ (curves 1 & 2) and $\max \nu_6$ (curves 3 & 4) on partial Cl_2 pressure (curves 1 & 3) for a mixture 1 torr $\text{H}_2 + p$ torr $\text{Cl}_2 + 10$ torr He and on partial H_2 pressure (curves 2 & 4) for a mixture 1 torr $\text{Cl}_2 + p$ torr $\text{H}_2 + 10$ torr He ($A=10^9$, $\tau=10^{-4}$ sec).

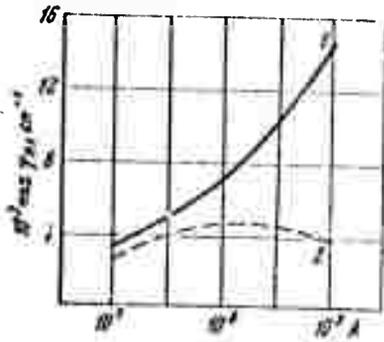


Fig. 22. Dependence of gain $\max \nu_2$ (curve 1) and $\max \nu_6$ (curve 2) on the flash amplitude A (original mixture as in Fig. 17).

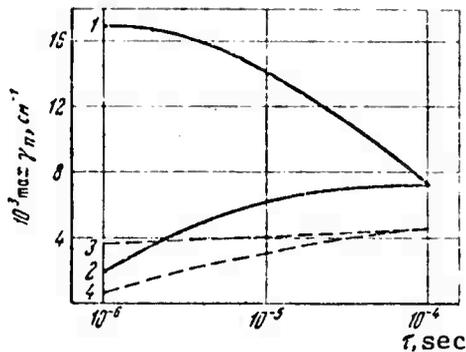


Fig. 23. Dependence of gain $\max \nu_2$ (curves 1 & 2) and $\max \nu_6$ (curves 3 & 4) on the characteristic time of flash τ at a constant total flash energy (curves 1 & 3, $A\tau^2 = \text{const} = 1$) and a constant maximum flash power (curves 2 & 4, $A\tau = \text{const} = 10^4$). Original mixture parameters same as in Fig. 17.

iii. Vibrational Energy Relaxation

In a recent paper, Orayevskiy used rate equations to analyze the effects of resonance radiation on the explosion limits.¹⁸ This approach -- demonstrated on the example of thermally excited $\text{H}_2 + \text{Cl}_2$ -- enabled him to write the equation for the ignition limits containing the relaxation rate constants of the excited states. The usefulness of this equation is that it points to the possibility of decelerating the reaction by the resonance radiation.

The kinetics of such a process involves the excitation of the working levels, their relaxation, and the stimulated transitions. The rate

equations which describe these are

$$\frac{dx^*}{dt} = \sigma_1 e^\theta - \sigma_{21} x^* + \sigma_2 (x^* - x) \quad (16)$$

$$\frac{dx}{dt} = \sigma_{21} x^* + \sigma_2 (x^* - x) + \sigma_{10} x \quad (17)$$

$$\frac{d\theta}{dt} = \sigma_3 e^\theta - \sigma_4 \theta + \sigma_5 x^* + \sigma_6 x \quad (18)$$

where x^* and x are the populations of upper and lower levels, respectively; $\sigma_1 = k e^{-E/RT} \rho^n$ is the rate of the chemical reaction at an initial temperature ($W_1 = \sigma_1 e^\theta$); $k e^{-E/RT}$ is the reaction rate; ρ is the mixture concentration; n is the kinetic order of reaction; $\sigma_{21} = k_R \rho$ is the relaxation rate ($W_2 = \sigma_{21} x^*$); $\sigma_2 = BI$ is the rate of radiative transitions, B is the Einstein coefficient; σ_{10} is the relaxation rate of the lower laser level; $\sigma_3 = (1-\eta) \frac{Q}{c} \frac{E}{RT} \cdot \frac{1}{\rho} \sigma$ is the initial rate of heat liberation; $(1-\eta)$ is the portion of energy distributed over the $V-T$ degrees of freedom of the reaction products; c is specific heat; $\sigma_4 = hS/\rho cV$ characterizes heat liberation, where S is the surface area, V the volume and h is coefficient of heat transfer; $\sigma_5 = \eta \frac{Q}{c} \frac{E}{RT} \cdot \frac{1}{\rho} \cdot \sigma_{21}$ is the rate of heat liberation during the relaxation.

The critical condition for ignition can be expressed as follows:

$$G = \sigma_3 + \frac{\sigma_1 \sigma_5}{\sigma_{21}} x(\sigma_2) + \frac{\sigma_1 \sigma_6}{\sigma_{10}} - \frac{\sigma_4}{e} = 0, \quad (19)$$

where

$$x(\sigma_2) = \frac{\sigma_{21} \sigma_2 + \sigma_{10}}{\sigma_{10} \sigma_2 + \sigma_{21}} \quad (20)$$

Let

$$g = \sigma_3 + \frac{\sigma_1 \sigma_5}{\sigma_{21}} + \frac{\sigma_1 \sigma_6}{\sigma_{10}} - \frac{\sigma_4}{e} \quad (21)$$

be the ignition limit threshold coefficient.

It follows from (19) that the radiation causes shifts in the ignition limit. This effect can be useful or detrimental, depending on the relationship between kinetic constants of relaxation. The significant feature of this effect is the existence of a threshold defined by the radiation intensity. If

$$\sigma_{10} > \sigma_{21} \quad (22)$$

and

$$\sigma_2 > \left[\frac{\sigma_{10}}{\sigma_{21}} \left(1 - \frac{\sigma_{21}}{\sigma_1 \sigma_5} g \right) - 1 \right]^{-1} \frac{\sigma_{10} \sigma_{21}}{\sigma_1 \sigma_5} g, \quad (23)$$

then $G < 0$ and an explosion fails to take place even if the condition for its occurrence is fulfilled ($g > 0$). In such a case, the reaction is terminated by the radiation. However, the reaction can be arrested if and only if

$$g < \frac{\sigma_1 \sigma_5}{\sigma_{21}} (1 - \kappa(\infty)), \quad (24)$$

where $\kappa(\infty) = \sigma_{21} / \sigma_{10}$.

When

$$\sigma_{21} > \sigma_{10}, \quad (25)$$

the reaction is accelerated by the radiation. In particular, when $G > 0$ the stationary temperature regime cannot be achieved even if $g < 0$ in the absence of radiation. This occurs when

$$g > - \frac{\sigma_1 \sigma_5}{\sigma_{21}} [\kappa(\infty) - 1] \quad (26)$$

and the excitation intensity is greater above threshold (Eq. 23).

The picture which emerges from the physical interpretation of the above equations is as follows. If Eq. (22) is satisfied, the pumping radiation is amplified, and a portion of the energy is coupled out of the reaction region in the form of stimulated emission. The existence of the lower intensity limit of radiation which is capable of inhibiting the reaction (Eq. 23), can be explained in terms of a competition between the extraction of energy and the relaxation process which tends to thermalize this energy. Since the stimulated transition

cross-section is low at very small excitation intensities, nearly all the exothermic energy is used to heat the mixture. If $g > (1-\kappa(\infty))\sigma_1\sigma_5/\sigma_{21}$, the amount of heat evolved in the system is so large that an explosion occurs even at infinitely high fluxes for which the maximum possible laser energy is coupled out of the system.

If $\sigma_{21} > \sigma_{10}$, only the absorption of incident radiation is possible in the steady state. At above-threshold light intensities (23), the incident radiation causes thermal explosion in a certain pre-ignition range of values of g (26). If

$$g < -(\kappa(\infty) - 1)\sigma_1\sigma_5/\sigma_{21}, \quad (27)$$

the heating of the mixture due to radiation absorption is insufficient to create explosion even for an infinitely strong optical flux. Under such conditions, the reaction proceeds in a steady state fashion.

As the vibrational numbers increase the cross section of converting the vibrational energy into translational increases. In the context of Orayevskiy's system, this means that $\sigma_{21} > \sigma_{10}$, if the relaxation of the excited levels is directly due to the scattering of the vibrational energy into the translational degrees of freedom. In such systems, the effect of radiation is capable of initiating only the thermal explosion.

The satisfaction of the condition $\sigma_{10} > \sigma_{21}$ is associated with a search for mixtures in which an effective deactivation of the lower working level takes place. The effectiveness of this process is partly determined by the resonance of vibrational frequency of the colliding molecules. As an example of this, there occurs an effective depopulation of the HF($v = 1$) level due to $1 \rightarrow 0$ quasi-resonant vibrational transitions of H_2 ($\nu_{10} = 4161 \text{ cm}^{-1}$) and HF ($\nu_{10} = 3962 \text{ cm}^{-1}$) molecules.

Orayevskiy's system is, by his own admission, not general. It can be modified to allow for energy transfer from "hot" reaction products to "cold" molecules of diluent. This was demonstrated by Basov¹⁹ and Khokhov²⁰ in the case of $HN_3 + CO_2$ mixtures. Orayevskiy claims that if in such systems the energy transfer is sufficiently

effective -- which Basov and Khokhov say it is -- and if the diluent molecules which receive the vibrational energy, can satisfy the condition $\sigma_{10} > \sigma_{21}$, then the effect of radiation on such molecules should decelerate the reaction.

The inhibition of reaction can occur in the course of laser action when the reagents are placed inside the optical cavity. This effect appears to be particularly pronounced in the case of branched chain reactions. As examples of this are the reactions in $H_2 + F_2$ and $D_2 + F_2$ mixtures. The reaction deceleration in such mixtures occurs due to depopulation of the upper levels of excited molecules responsible for branching. Although such an effect was recently considered by Dolgov-Savel'yev for an $H_2 + F_2$ system,¹⁴ Orayevskiy's paper has the distinction of being the first to reveal the heretofore unknown Soviet interest in the DF molecule.

3. Discharge vs. Photolytic Excitation

What then are the significant differences, if any, between electric discharge and photolytic excitation of the same mixture? The principal difference, according to Dolgov-Savel'yev,¹⁴ is the fact that electric-discharge pumping produces surprisingly long chemiluminescence pulses and a short laser pulse. However, the shape of the latter resembles that obtained under photolytic initiation, particularly in the early stages.

C. POLYATOMIC SYSTEMS

The arguments in support of utilizing polyatomic molecules in chemical lasers relate to their property of having energy-level systems with different temperatures and a long relaxation which is favorable to producing a population inversion.

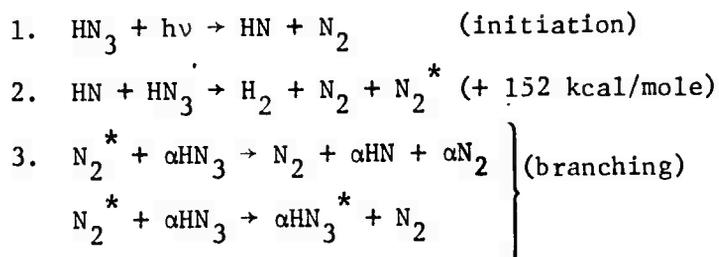
The population inversion in polyatomic (molecular) systems was the subject of several Soviet studies; the most prominent among these were Basov's, showing the possibility of inverting CO_2 molecules in an $N_2 + CO_2$ mixture escaping into a vacuum. Thermally pumped molecular

lasers -- such as Basov's GDL -- are, however, outside the scope of this paper and will not be discussed here.

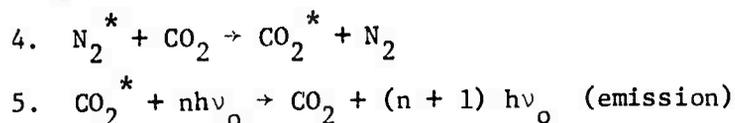
1. HN₃ + CO₂ Experiments

a. With Photolytic Initiation

A quasi-chemical explosion laser based on the decomposition of the HN₃ molecule in an HN₃ + CO₂ mixture was demonstrated by Basov in mid-1969.¹⁹ The mixture was pumped by a xenon flash lamp with energies up to 1 kJ in a quartz tube 1.5 m long and 30 mm in diameter. The Au-coated optics was provided with a 1.5 mm dia. aperture for energy extraction. The HN₃ was produced directly in a special section of the setup, from the reaction between sodium azide and sulfuric acid followed by purification. The decomposition of HN₃ was a branched chain reaction with the following sequence:



The vibrationally excited ("hot") nitrogen then transferred its energy to the ("cold") CO₂ molecule as follows:



where n is the number of photons at a laser frequency ν_0 .

The emission signal from the reaction was observed ~250 μ sec after triggering and is shown in Fig. 24. The wavelength of this emission was $\lambda > 7\mu$. The pulsations in the laser output -- which disappeared when the resonator was detuned -- were the result of transient processes occurring in a medium which has a relaxation time shorter than the photon lifetime in the cavity.

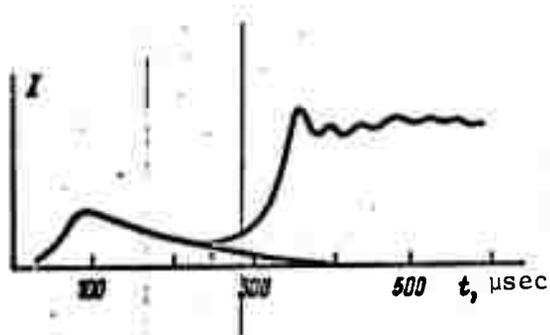


Fig. 24. Laser pulse in an $\text{HN}_3 + \text{CO}_2$ mixture

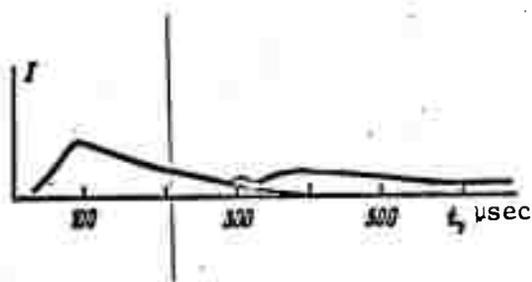


Fig. 25. Laser pulse in HN_3 without CO_2

As a control experiment, the HN_3 was exploded in the absence of CO_2 . The corresponding oscillogram of the trigger and output pulses is shown in Fig. 25. The output pulse which follows the triggering 300 μsec later is apparently the chemiluminescence of the vibrationally excited HN radical. The spectral region of this emission was $\sim 4\mu$.

b. With Discharge Initiation

The experiments with $\text{HN}_3 + \text{CO}_2$ mixtures were also performed by the Khokhlov group²⁰ and appear to be more comprehensive than Basov's. The basic difference between the two sets of experiments was the pulse initiation method which, in Khokhlov's case, was electric discharge. An attempt was made in Khokhlov's study to measure the vibrational and rotational temperatures of CO_2 molecules produced in the chemical reaction.

The experimental setup is shown in Fig. 26.

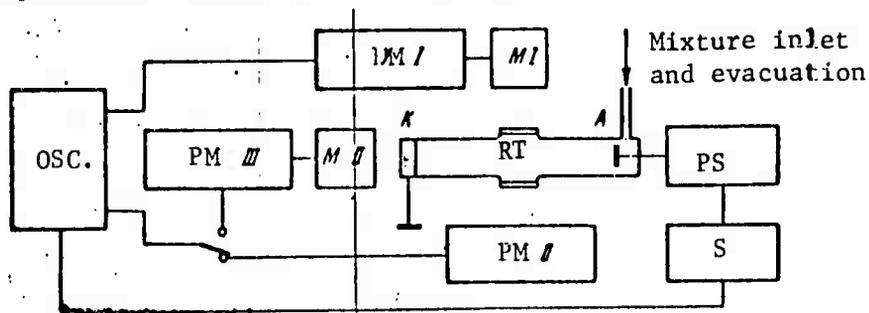


Fig. 26. Bloc diagram of experimental setup. RT - reaction tube; PM - photomultiplier & detector; M - monochromator; PS - pumping source; S - synchronization; K,A - electrodes.

The mixture (HN_3 partial pressures 2-5 torr) entered a glass tube 50 cm long and 5 cm in diameter, and was triggered by a 1 -- 2- μsec 0.7-j electric pulse. The tube featured two symmetrical side and one end fluoride windows. The beam was extracted through one of the side windows and was directed onto the slit of monochromator M I and was recorded by a Ge:Au detector (FM I) cooled to 77°K. The signal was fed to a dual-beam oscillograph, to which the second -- control -- channel was hooked up to operate in the 2 -- 7 μ region. The measurements were carried out in the 2400 -- 2100 cm^{-1} region in 14 cm^{-1} intervals for a 6 cm^{-1} spectral slit. The second monochromator M II with an identical detection system was used to monitor emission in the 2.6 μ range and for evaluating the effect of self-absorption in the 4.3 μ region.

Two types of mixtures were used: 3 HN_3 + 1 CO_2 and 3 HN_3 + 1 CO_2 + 8 Ar at the total pressures of 7 and 21 torr , respectively. The time constant of the equipment in the first case was 15 μsec . In the case of an argon-doped mixture, the M II channel time constant was 100 μsec . The signal-to-noise ratio in the 2100 -- 2360 cm^{-1} region was not less than 10; in the 2360 -- 2400 cm^{-1} region, it decreased rapidly with ν (down to 2 when the time constant was 15 μsec). The discharge and reaction in the 3 HN_3 + 1 CO_2 mixture were spatially inhomogeneous. The M I channel output fluctuated rapidly with time with respect to the envelope and from explosion to explosion within 30%. Although these fluctuations tended to subside at lower triggering energies, the output was far from steady (Fig. 27).

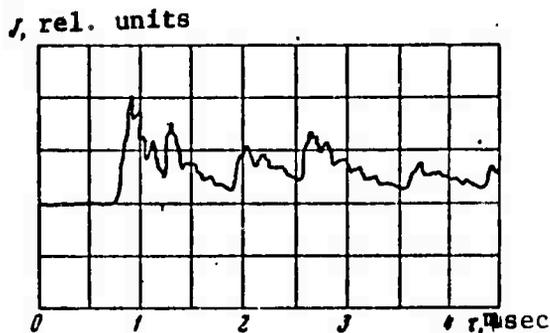


Fig. 27. Signal from channel I in the case of nonhomogeneous initiation of 3 HN_3 + 1 CO_2 mixture.

The origin of the spikes was traced to the following process. The reaction develops at first near the tube walls and proceeds, together with the emission, towards the tube axis. As a result of this, strong acoustic waves are set up which distort the reaction path and complicate the energy distribution pattern.

The addition of argon to the $\text{HN}_3 + \text{CO}_2$ mixture tends to spatially homogenize the triggering. The output from detector PM II for an argon-doped mixture is shown in Fig. 28.

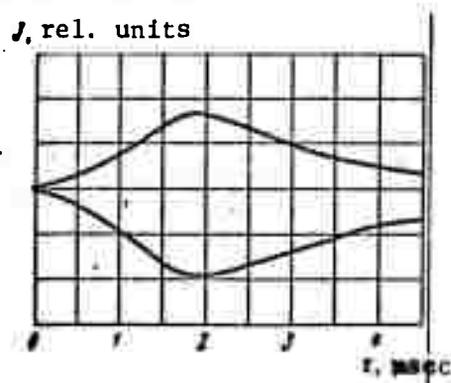


Fig. 28. Signal from control channel II (lower curve) and channel I (upper curve) in the case of explosion of $3 \text{HN}_3 + 1 \text{CO}_2 + 8 \text{Ar}$ mixture.

Measurements showed that the total beam intensity was more than one order of magnitude higher at 4.3μ than at 2.6μ . Thus, for vibrational temperatures greater than the Debye temperature, the total intensity measured at PM II is approximately proportional to T_3 . Therefore, $T_3(t) \sim J_{\text{contr}}(t)$, where J_{contr} is the intensity measured by PM II. This relationship holds only in the absence of density fluctuations, which was precisely the case with the Ar-doped mixture.

The frequency dependence of the beam intensity $J(\nu)$ in the $2100 - 2400 \text{ cm}^{-1}$ region at $\tau = 1.5$ and 2 msec is shown in Fig. 29.

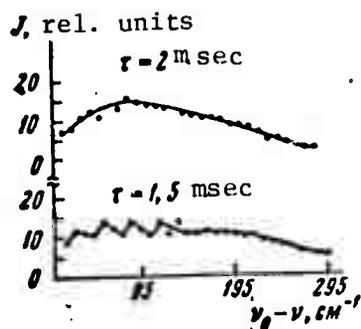


Fig. 29. Spectral dependence of CO_2 intensity on frequency in the case of explosion in a $3 \text{HN}_3 + 1 \text{CO}_2 + 8 \text{Ar}$ mixture at different τ .

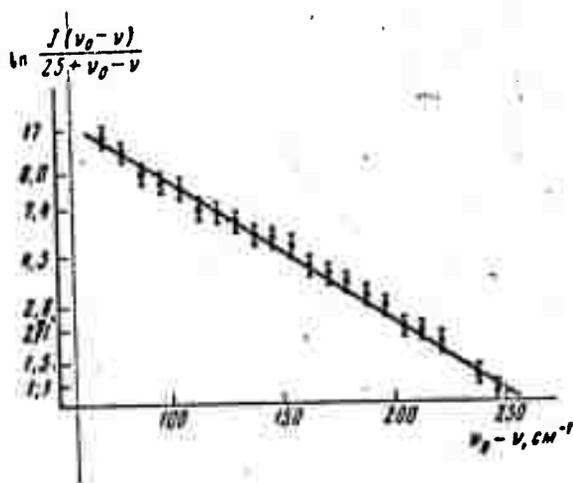


Fig. 30. Dependence of $\log_e [J(\nu)/(25 + \nu_0 - \nu)]$ on frequency for the same mixture as Fig. 29 and $\tau = 2 \text{msec}$.

In the initial stages the function $J(\nu)$ is not piecewise continuous and the maxima correspond to transitions $0, 0, \nu + 1 \rightarrow 0, 0, \nu$. In this region $J(\nu) \sim (a + x)e^{-\beta x}$ which implies that $T_3 > T_2 \times 23^{\nu_2} / 2 \times 33^{\nu_2} \approx 1.55 T_2$. As the rotational (and T_2) temperatures increase, the solution deteriorates. At $\tau = 2 \text{msec}$, $J(\nu) \sim (a + \nu_0 - \nu) \exp[-\beta(\nu_0 - \nu)]$, where $a = 25 \text{cm}^{-1}$ and $\beta = 90 \text{cm}$. The values of β and, consequently, T_3 were determined from the slope of the straight line $\log_e [J(\nu)/(25 + \nu_0 - \nu)]$ (Fig. 30).

Thus, at $\tau = 2 \text{msec}$, $T_3 = 3.60 \theta \approx 12,000^\circ (\pm 10\%)$.

The rotational temperature T_{rot} was determined from the slope of the curve in Fig. 31 in the $2360 \text{--} 2400 \text{cm}^{-1}$ range (corresponding to the R-branch of the $100\text{--}000$ transition). The experimental accuracy was only 50% due to the small signal-to-noise ratio.

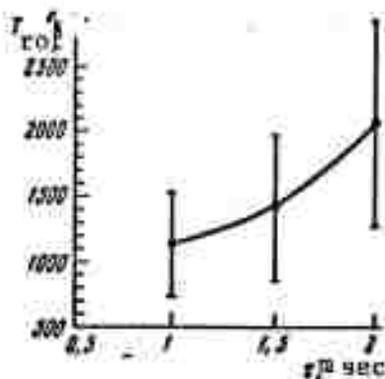
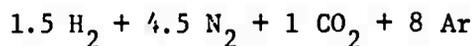


Fig. 31. Temporal dependence of rotational temperature T_{rot} in a $3 \text{ HN}_3 + 1 \text{ CO}_2 + 8 \text{ Ar}$ mixture.

Because of the insufficiently accurate measurements no direct readings were made of the vibrational temperature T_2 . However, the upper limit of T_2 was determined from the energy output of the reaction and from T_3 and T_{rot} . For $\tau = 2 \text{ msec}$, $T_2 < 3000^\circ$, further assuming that the vibrational temperatures of the nitrogen and hydrogen were nearly equal to T_3 . Thus, knowing that the relaxation rate of the symmetrical and deformed modes is high, Khokhlov assumed that $T_2 \approx T_{rot}$.

In effect, the experiments showed that the ratio T_3/T_2 is sufficiently high to vibrationally invert the population in the system. However, due to high T_{rot} , T_2 and T_3 temperatures, the gain of the medium was small. Thus, in the following mixture:



and at $T_3 = 12,000^\circ$, $T_2 = 3000^\circ$ and $T_{rot} = 1200^\circ$ ($\tau = 1.25 \text{ msec}$), the maximum gain was 1% per meter. When $T_2 = T_{rot} = 1200^\circ$ and $T_3 = 12,000^\circ$, the gain was 10%/m.

c. With Hybrid Initiation

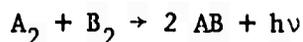
More recently, Khokhlov's group produced lasing at $\lambda = 10.6 \mu$ from the explosion of a $5 \text{ HN}_3 + \text{CO}_2 + 6 \text{ He}$ mixture pumped by a hybrid source.²¹ In this case, two coaxial quartz tubes were used, each 1 m long but of

different diameters -- 33 and 65 mm. The thinner ("internal") tube was truncated with mirrors and was filled with the working mixture, while the thicker ("external") tube contained HN_3 at a pressure of ~50 torr. The reaction in the "external" tube was triggered by a transverse discharge and the resultant light was used to initiate the reaction in the "internal" tube. Although the output energy was not measured, stimulated emission was observed in the working mixture at the pressure of 12 torr and 500 μsec after the explosion of HN_3 . The duration of the single pulse produced in this manner was ~200 μsec .

V. STIMULATED PHOTORECOMBINATION LASER

Pekar's entry into the chemical laser research a year ago occurred at a juncture when the following situation existed.²² In all the known chemical lasers -- operating without external pumping, strictly due to the chemical reaction energy -- the kinetic process consisted of two stages: 1) a common chemical reaction was taking place as a result of which excited molecules were produced without the aid of the stimulated emission, and 2) the stimulated emission of the excited molecules proceeded without a chemical reaction. The first stage tends to limit the rate and power of the laser emission by virtue of the weak common reaction, and is characterized by heating, thus leading to energy losses and, often, a catastrophic destruction of the experimental setup at high powers.

In view of the above disadvantages, Pekar proposed a laser of a different type in which the stimulated transition of electrons occurred at the very instant of contact between two unexcited reagents:



Such a radiative process -- recombination radiation of atoms -- in itself constitutes an elementary act of a chemical reaction, thus eliminating stages 1 and 2 described above and, under favorable conditions, it can be used to produce laser radiation.

In his calculations, Pekar assumed that there exists a region in which a pair of molecules is in physical contact and the cross-section of the spontaneous phototransition of electrons is high ($\sim 10^6 \text{ sec}^{-1}$), while elsewhere in the region it is zero. The number of simultaneously reacting molecule pairs in a 1 cm^3 volume is $\nu n_1 n_2$ (where n_1 and n_2 are the reactant concentrations) and $\nu = 10^{23} \text{ cm}^3$. If ω_m is the band maximum of the spontaneous emission and $\Delta\omega$ its effective width, then the number of modes in 1 cm^3 is $\omega_m^2 \Delta\omega / \pi^2 c^2$, where c is the velocity of light. If $n_1 = n_2 = n = 10^9 \text{ cm}^{-3}$, $\Delta\omega = 0.01 \omega_m$, $\omega_m = 3 \times 10^{15} \text{ sec}^{-1}$, the gain is

$$\alpha \sim \pi^2 c^2 \nu n_1 n_2 / \omega_m^2 \Delta\omega \sim 0.03 \text{ cm}^{-1}. \quad (28)$$

Pekar further assumed that the reaction products were either rapidly carried away or their concentration was negligible at the onset of the pulsed reaction. The above gain is sufficiently high to achieve laser action with or without resonant feedback, provided the linear dimensions of the volume filled with gas are sufficiently large ($>1/\alpha$). The gain can be also increased by increasing the concentration n .

If the reaction products are not removed, the reaction proceeds discretely and finally discontinues after nearly $n/2$ molecules have reacted. At the height of the reaction the number of working-mode photons per cm^3 is $n/4$. The rate of stimulated chemical reaction at that time is $nc/4 = 2.5 \times 10^{27} \text{ cm}^{-3} \cdot \text{sec}^{-1}$. The optical power is $\hbar\omega W \sim 7 \times 10^8 \text{ w} \cdot \text{cm}^{-3}$ and it is proportional to n^3 . The pulsed reaction time is proportional to n^{-3} and is on the order of 10^{-8} sec.

The situation can be represented by the potential energy curves in Fig. 32,

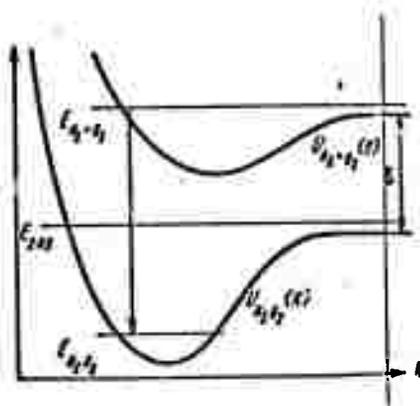


Fig. 32. Potential energy curves of a system of molecules.

where R is the set of coordinates of molecule pair nuclei, $U(R)$ is the potential energy of nuclei and E is the total energy of the system.

Immediately after the transition a four-atom system A_2B_2 is formed which then dissociates into $2AB$. The amount of heat required for the dissociation is $h\nu - \epsilon > 0$; this energy is extracted from the ambient gas, which cools rapidly during the reaction down to a certain temperature at which the dissociation ceases. The temperature then remains constant and no heat is evolved which can disrupt the laser and decrease its efficiency.

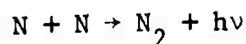
If $E_{A_2B_2}$ is the lowest vibrational level of the system, the gas continues to cool even after the dissociation ceases since the A_2B_2 molecules are at the absolute zero vibrational temperatures.

If the light absorption in the optics, Raman scattering at ν , and other effects are neglected, the light-induced chemical reaction can be achieved by a thermodynamically reversible process. The resultant optical energy will exceed the energy evolved in the combustion of fuel by an amount of $h\nu/\epsilon$ due to the heat removed from the surrounding medium.

Although Pekar's proposed laser appears to hold some interest as a means for speeding up chemical reactions -- or for initiating reactions which cannot be achieved by other means -- there are some difficulties in harnessing the photorecombination process to the production of stimulated emission. These, and other considerations concerning the achievement of the population inversion in such a laser are the subject of a recent paper by Orayevskiy.²³

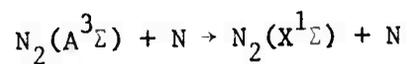
Orayevskiy considers Pekar's proposal feasible although a difficult one to achieve in practice. First, only the IR generation is possible along the diffusion layer; second, triple collisions, along which the reaction proceeds, ($A + B + M \rightarrow AB + M$, where M is any reacting particle in the mixture), tend to reduce the total number of particles in the diffusion layer as the density of reactants increases; and, third, the cross-section of recombination of chemically stable compounds is very small.

As a means of laser excitation Orayevskiy proposes heating the gas molecules to a temperature at which the dissociation is considerable and, subsequently, rapidly cooling the gas by conventional methods. As an example of this, Orayevskiy cites nitrogen, whose atoms recombine into $B^3\pi$ molecules as follows:



The rate of the emission of light occurs at $0.6 \times 10^{-17} (300/kT)^{0.9} N^2$ photons/sec from $N_2(B^3\pi) \rightarrow N_2(A^3\Sigma) + h\nu$. The $A^3\Sigma$ state is metastable

and has a long lifetime. It can be depopulated effectively due to collisions with the nitrogen atoms, a process which restores the molecule to the ground state:



at the rate of $5 \times 10^{-11} \text{ N}$. When the atom concentration N is $\sim 10^{18} \text{ cm}^{-3}$, the rate of the above process is greater than the rate of population of the $\text{A}^3\Sigma$ level due to excitation.

VI. CONTROLLED CHEMICAL REACTIONS

Tunable IR lasers are readily applicable to controlling the chemical reaction rates. Studies in this vein which are receiving serious consideration in Khokhlov's group,²⁴ postulate that the control over the reaction can be exercised in the form of resonant coupling of radiation to a given vibrational degree of freedom of a molecule followed by the selective "heating." The interaction tends to weaken a given bond and thus rapidly accelerates the reaction. In order that this may occur the vibrational temperature T_v must be much greater than the temperature of the remaining degrees of freedom T .

The parameters of a source which could be used to achieve the above were derived by Khokhlov for two special cases:

- 1) the pump pulse duration $t_0 \ll \tau_0$
- 2) the pump pulse duration $t_0 \gg \tau_0$

In the first case, the maximum vibrational temperature which can be obtained due to a short pulse is

$$T_v \text{ max} \approx \frac{h\nu}{T_0} [\ln(2+a)]^{-1}. \quad (29)$$

where

$$a = \exp\left(-\frac{E_{j_1} - E_{j_0}}{kT_0}\right). \quad (30)$$

and E_{j_1} and E_{j_0} are the rotational energies of levels 1 and 0, respectively. When $a \approx 1$ ($|E_{j_1} - E_{j_0}| \ll kT$), $T_v \text{ max} \approx h\nu/k$.

Assuming a rectangular pump pulse, the intensity I required to achieve $T_v \text{ max}$ is

$$I \gg \frac{4\pi^2\tau\delta h\nu^3}{c^2n(j_1)} \frac{1}{t_0} \gg \frac{4\pi^2\tau\delta^0 h\nu^3}{c^2n(j_1)} \frac{1}{\tau_0^0} p^2. \quad (31)$$

where p is the gas pressure, δ^0 and τ_0^0 are the line halfwidth and v-v relaxation, respectively, reduced to a unit pressure, i.e., $\delta = \delta^0 p$ and $1/\tau_0 = p/\tau_0^0$. Assuming $\tau \approx 10^{-2}$ sec, and 3×10^{-3} sec for CO_2 and N_2O

molecules, respectively, $\tau_0 \approx 10^{-5}$ sec.torr and $\delta = 5 \times 10^6$ sec $^{-1}$.torr for both the molecules, and $n(j)$ being equal to the maximum population of the rotational level at $T_0 = 300^\circ\text{K}$, the numerical value of the p^2 multiplier in the above equation was nearly 3×10^{-3} w.cm $^{-2}$.torr $^{-2}$ for both the CO_2 ($\nu_3 = 2349$ cm $^{-1}$) and N_2O ($\nu = 2223$ cm $^{-1}$) molecules.

Thus, for both CO_2 and N_2O , the required intensity at the atmospheric pressure will amount to several tens of kw.cm $^{-2}$.

In the case of the cross-relaxation being considerably longer than the pump pulse, the vibrational temperature is given by the following expression

if $a > 1$ (P-branch)

$$T_v < \frac{h\nu}{k} \ln a = \frac{h\nu}{E_j - E_i} T_0. \quad (32)$$

and for $a \approx 1$

$$T_v \approx 2500-2700^\circ\text{K}$$

Assuming $\tau_1 / \tau_0 \sim 100$, the corresponding intensities are

$$I = I_0 p^2, \quad (33)$$

(where $I_0 \approx 3 \times 10^{-3}$ w.cm $^{-2}$.torr $^{-2}$) and for the CO_2 and N_2O molecules, amount to ~ 30 w/cm 2 at pressures on the order of 100 torr. For CO , the corresponding intensity is ~ 2 w/cm 2 .

In the case of a reaction $\text{N}_2\text{O} + \text{NO}$ the rate of change of partial pressure is

$$\frac{1}{p_{\text{NO}}} \frac{\partial p_{\text{NO}}}{\partial t} = K_0 e^{-E_a/hT_0}. \quad (34)$$

Assuming the rate of the backward reaction to be small, it can be said

that rate of the $N_2O + NO$ reaction is determined basically by the vibrational temperature of N_2O with a frequency of $\nu_3 \approx 2223 \text{ cm}^{-1}$. That is to say, T_o can be replaced by T_v in the above equation. As an example, Khokhlov calculated T_v° for which the left-hand side of Eq. 34 is $> 1/\tau_1$, obtaining

$$T_v^\circ \approx E_a/kT_o \log_e K_o \tau_1^\circ \quad (35)$$

At $T_o = 300^\circ\text{K}$, $K_o = 2 \times 10^7 \text{ sec}^{-1} \cdot \text{torr}$ and $T_v^\circ = 2500^\circ\text{K}$.

The foregoing indicates that such temperatures are feasible at intensities which are possible in practice. Moreover, since the reaction occurs during a time much shorter than the cross-relaxation, the kinetic temperature T_o , remains constant throughout the reaction. Thus, being selective the pumping radiation accelerates only those processes whose cross-section depends essentially on the temperature of a given degree of freedom.

VII. THE SUMMARY OF CURRENT SOVIET ACCOMPLISHMENTS

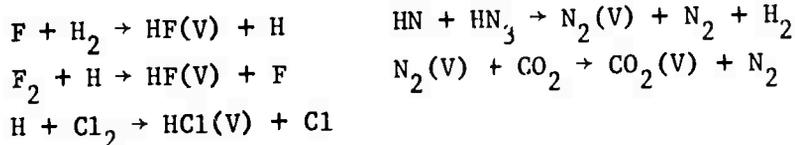
The Soviet advances in the chemical laser field will be summarized below in an order which does not necessarily reflect the degree of priority.

A. Spectral studies were made of the beam composition, yielding useful information on:

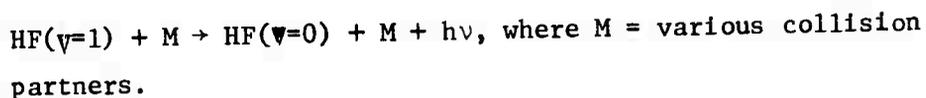
1. the energy distribution of the various V-R levels;
2. excitation and relaxation mechanisms in a laser.

B. Analytical models of cw chemical lasers were developed and the experience gained was applied to the understanding of pulsed chemical lasers; the following were studied theoretically:

1. Chemical Reaction Kinetics



2. V-T Transfer Kinetics



C. Extensive theoretical studies to estimate V and R relaxation rates in $H_2 + F_2$ and $H_2 + Cl_2$ systems were undertaken.

D. Laser pulse initiation techniques were analyzed.

1. Comprehensive theoretical and experimental research was made on the explosion limits in the $H_2 + F_2$ system. This involved studying the effects of additives and diluents on the explosion limits. The chain branching as a laser mechanism was thoroughly studied for $H_2 + F_2$, $H_2 + Cl$ and other mixtures.

2. Use was made of absorbers (Ar, Xe) in the mixture to spatially homogenize the triggering.
3. Electron beam, pulsed electric discharge, flash photolysis and hybrid triggering systems -- consisting of the two latter -- were used to successfully produce laser pulses.
4. Experiments were carried out with high-energy electron beams as a means for rapid uniform volumetric initiation of a reaction. Nothing is known about the Soviet uses of pre-ionization techniques to achieve the same as above; however, they have been experimenting with hybrid electron beam-electric discharge pumping methods in $\text{CO}_2 + \text{Ar}$ and $\text{CO}_2 + \text{Xe}$ mixtures and deriving from these noticeably increased output powers.

E. Not much appears to have been done on flowing gas mixtures such as Cool's $\text{NO} + \text{F}_2$, which dispenses with either flash photolysis or arc heater initiation of HF reactions. Nevertheless, the Soviets proposed a flowing cw optically-pumped CO_2 laser in which the working mixture is doped with an alkali metal vapor also contained in the flash lamp. The vibrationally inverted CO_2 is expected to produce extractable cw powers of 100w/m for ~10% efficiency, i.e., an effort comparable to a conventional sealed-off discharge CO_2 laser. Although, the Soviets have done nothing so far on the promising CO laser obtained from $\text{CS}_2 + \text{O}$ mixtures, they are underscoring the feasibility of the above-proposed optical pumping technique to excitation of a CO laser operating at 5 μ .

F. A proposal was made to build a chemical laser based on photo-recombination of atoms.

G. Use of resonant excitation of vibrational levels followed by a selective heating was proposed as a means of controlling the rate of a chemical reaction.

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